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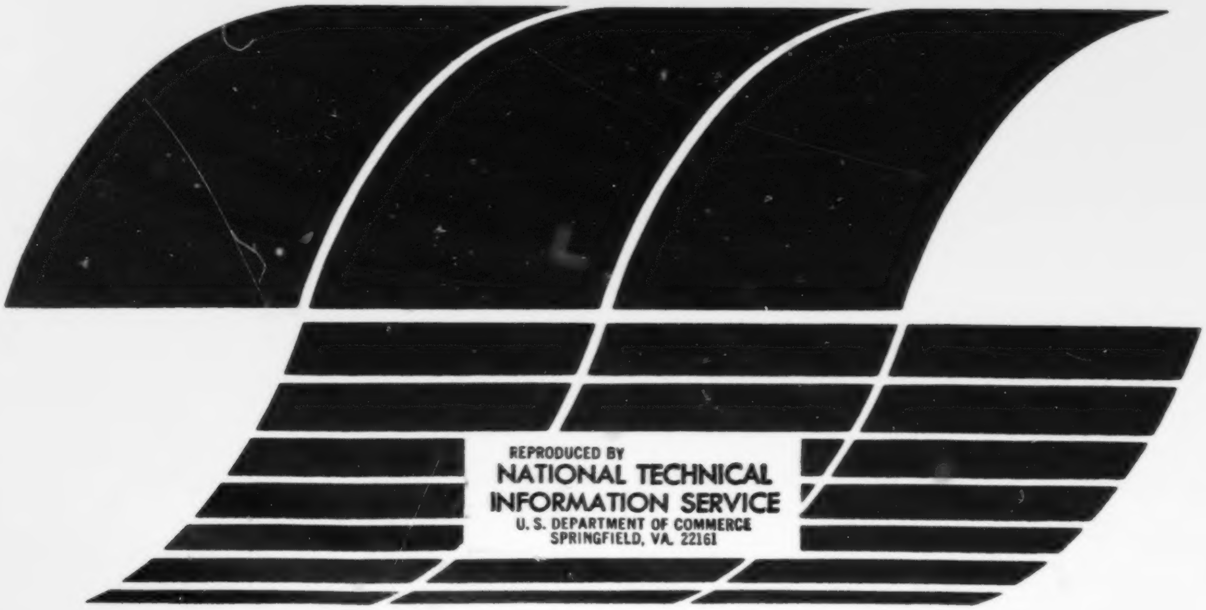

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Liquefaction	Water Treatment	Byproduct Coke Oven Process	07D	
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ABSTRACT

Since there appear to be many similarities in the product, byproduct and wastestream characteristics between the coke oven and coal conversion processes, Catalytic, Inc. has been directed to conduct this study to review coke oven processes and control technologies and to assess their applicability to the coal conversion (synfuels) industry.

Most of the major coke oven and coal conversion processes have been considered, with special emphasis on: Lurgi, Koppers-Totzek, SRC-I, COED, Synthane and Byproduct coke oven processes. Detailed material balances are given for commercial size Byproduct coke oven and SRC-1 processes. Comparisons of the process and waste stream characteristics from the Byproduct coke oven process with selected gasification and liquefaction processes have been made; and recommendations regarding control technologies are suggested for air, water and solid wastes. An extensive review of coke oven control technology was made. State and Federal regulations concerning the disposal and treatment of coke oven wastes are presented along with a brief assessment of health effects attributed to the coke oven emissions.

The results of the study indicate that a number of coke oven control technologies are applicable to coal conversion systems, especially those dealing with desulfurization, fugitive emissions, byproduct recovery/upgrading and wastewater treatment. Byproduct upgrading and fugitive emission control technologies might be readily transferrable to analogous coal conversion applications. Desulfurization and wastewater treatment technologies, however, could not be readily transferrable to those applications where significant differences exist in the composition, temperature and pressure of the two categories of process/waste streams. In these cases, laboratory or pilot plant scale tests will be required with actual coal conversion wastes to determine the design bases and the treatability variations between the coal conversion and the comparable coke oven streams.

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SECTION 1

SUMMARY AND CONCLUSIONS

Coal was once the major source of organic chemicals (chiefly aromatics) produced via the upgrading of coke oven byproducts. In recent years, these chemicals have been primarily supplied by processing petroleum and petrochemicals. In the future, as the coal gasification and liquefaction (coal conversion) industry grows, it is expected that increasing amounts of these chemicals will again be generated from coal.

Since there appear to be many similarities in the product, byproduct and wastestream characteristics between the coke oven and coal conversion processes, Catalytic, Inc. has been directed to conduct this study to review coke oven processes and control technologies and to assess their applicability to the coal conversion (synfuels) industry.

Most of the process information, waste stream characteristics and control technology data for the study were obtained from published literature. Some were generated by consultations with process vendors and coke oven plant operators and representatives.

Coke is produced by destructive distillation (carbonization) of low sulfur, bituminous coal in an oven or retort in the absence of air. Coal used in coke making is usually a blend of high-volatile coal with a 10 to 50 percent low-volatile coal; the blend should not contain over 1.5 percent sulfur or 9 percent ash. Approximately 16 percent of the bituminous coal mined in the U.S. is converted to coke which is used principally in blast furnaces and foundries. More than 98 percent of the total U.S. coke is produced from byproduct coke oven systems. The Byproduct process is oriented toward the recovery of the gases and chemicals produced during the coking cycle.

The major unit operations/processes involved in the Byproduct coke plant are: coal handling and preparation, coking, quenching, primary cooling, tar separation, tar extraction, ammonia removal, final cooling, light oil scrubbing, and sulfur removal (desulfurization). In addition, some modern coke plants have chemical refining (upgrading) facilities for recovery of benzene, toluene and xylene (BTX) from light oils.

The core of the process is the coke ovens, which are narrow chambers, usually about 38 to 50 feet long, 13 to 16 feet high, tapering in width from 17 to 20 inches at one end to 15 to 16 inches at the other. The ovens hold from 16 to 24 tons of coal, and are usually built in batteries averaging from 80 to 100 ovens. Although coke production from each oven is basically a batch process, a coke oven plant is operated such that the battery of ovens continuously produce coke oven gas and byproduct chemicals. In the Byproduct coke oven process, coking is accomplished at temperatures of 1,090 to 1,150°C and atmospheric pressure for a period of 16 to 27 hours.

One ton of the low sulfur bituminous coal (approximately 30% volatile matter, wet and on an "as received" basis) fed into a Byproduct coke oven will yield following products and byproducts:

	Quantity, lbs.
Coke	1,430
Coke breeze	93
Tar	78
Ammonia, anhydrous	5
Light oil	20
Gas, 10,350 scf	309
Water	65
	2,000

The principal subdivisions of coal gasification processes are low-, intermediate-, and high-temperature operations. These are further subdivided by operating pressures. The low-temperature gasification processes tend to show a complete product and byproduct slate, including oils, tars, and phenols. As the gasification temperature increases, the quantity of oils, tars and phenol decreases in preference to lighter products. The operating pressure also affects the yields. As the pressure increases, the product slate becomes heavier. For example, in intermediate-temperature processes, recoverable products such as naphthas and tars increase from zero or negligible quantities to significant quantities of heavier molecular weight chemical compounds.

Although the Byproduct coke oven process is vastly different from the gasification processes, many similarities appear to exist between the product and byproduct slates of the two industries. Therefore, it was theorized that the characteristic waste materials from the two industries may be similar. The report shows that this is true to some extent, but wide variations in quantities and compositional changes are evident, making comparative generalizations difficult.

The coal liquefaction processes are significantly different from the coal gasification processes, and, again, markedly different from the coke oven processes. Yet, the products and byproducts of the coal liquefaction processes show many similarities to those from Byproduct coke oven process. All liquefaction processes produce an acid gas stream which contains sulfur and other contaminants similar to the raw gases from the coke oven or coal gasification processes. Consequently, H_2S removal, including sulfur recovery, will be required for all coal conversion processes. This control technology is practiced by many coke oven plants. The aqueous waste streams of the coal liquefaction processes contain pollutants similar to the coke oven industry, and the accepted wastewater control technologies utilized in the coke oven industry should be applicable.

Table 1-1 provides a comparative listing of coke oven and coal conversion process and waste streams. Although many similar constituents are present in the various streams, their concentrations, temperatures and pressures are different (e.g., see Table 1-2 for raw gas compositions). These are important variables that will control the selection of the best available control technology for a particular stream. For example, note in Table 1-2, the ratio of CO_2 to H_2S in the streams. For the Lurgi and Koppers-Totzek (K-T) gasification processes, the ratio is much higher than either the coke oven or the Solvent Refined Coal (SRC-I) liquefaction process streams. High CO_2/H_2S ratios make sulfur removal and recovery more difficult in the gasification processes.

A number of processes are being utilized to remove hydrogen sulfide and recover sulfur from coke oven gas. These processes are divided into three major categories: 1) Liquid Absorption processes (Vacuum Carbonate, Sulfiban (amine type), Firma Carl Still); 2) Wet Oxidative processes (Stretford, Takahax,

TABLE 1-1. COKE OVEN AND COAL CONVERSION STREAM SIMILARITIES

Coke Oven Streams	Coal Conversion Counterparts	Major Common Pollutants or Similarities
Raw gas and acid gas	Raw gas and acid gas from gasification, and off-gas from liquefaction	H_2S, NH_3, CO, CO_2, COS, HCN and hydrocarbons
Process wastewater	Process wastewater	NH_3, phenols, oils, sulfides and cyanides (See Table 1-3 for details)
Coal pile run-off	Coal pile run-off	Suspended solids and organic extracts
Coke breeze	Coal fines, chars	Similar byproducts
Oily and biosludges	Oily and biosludges	Oil, grease and tar, biomass, refractory organics
Tar, naphthalene, light oil, phenol and ammonia	Tar, naphthalene light oil, phenol and ammonia	Similar byproducts
Fugitive emissions	Fugitive emissions	
. Coal pile	. Coal pile	Particulates
. Coal charging and coke pushing	. Coal lockhopper vent gases	Raw gas pollutants and particulates
. Coke quenching	. Ash/char quenching	Same as above
. Byproduct recovery and storage	. Byproduct recovery and storage	Odors, NH_3, H_2S, hydrocarbons and particulates
. Wastewater treatment	. Wastewater treatment	Same as above

TABLE 1-2. COMPARISON OF RAW GASES(1)

Components/Parameters	Lurgi(2)	K-T(3)	SRC-I Off Gas(4)	Coke Oven(5)
H_2	22.63	26.37	31.58	38.22
C_1	6.75	-	36.39	25.51
C_2	0.23	-	7.86	2.99
C_3 to C_5	-	-	5.81	-
CO	11.65	51.79	0.22	6.18
CO_2	16.16	8.82	3.84	1.33
O_2	-	-	-	1.26
N_2	0.18	0.69	0.43	0.452
NH_3	0.55	0.08	-	0.70
HCN	0.16	0.02	-	0.16
H_2S	0.203	0.41	12.68	0.51
COS	0.007	0.04	-	0.018
CS_2	-	-	-	0.01
Light Oil	0.14	-	1.19	0.79
Tar Oil	0.11	-	-	-
Tar	0.10	-	-	0.78
Phenol	0.05	-	-	0.04
H_2O	41.07	11.78	-	21.05
TOTAL	100.00	100.00	100.00	100.00
Temp., °F	370	2,730	119	1,000
Pressure, psia	450	15.3	24.7	14.3
Co_2/H_2S	79.6	21.5	0.303	2.6

1. Except as noted, all values are in vol %.
2. Sub-bituminous coal, El-Paso Lurgi process design. Bibliography 59.
3. Texas lignite feed containing 1.5% sulfur, 8% moisture. Koppers-Totzek gasifier.
4. One of the off-gas streams from the Solvent Refined Coal process. See other off-gases in Table 6-5.
5. Bituminous coal mixture suitable for coking; 1.0% sulfur, 4% moisture.

Giammarco Vetrocoke); and 3) The Dry Oxidative process (Iron Oxide or Dry Box). Historically, the Dry Oxidative process using iron oxide has been used most extensively. However, the Vacuum Carbonate process, the Stretford process and, more recently, the Sulfiban process have moved into commercial prominence.

The Liquid Absorption processes are called sulfur removal processes, since they remove sulfur compounds (e.g., H_2S) from the raw gas by liquid scrubbing and generally produce a gaseous stream more concentrated in H_2S (during regeneration of the solvent). The concentrated stream requires control via a sulfur recovery system - the Claus sulfur recovery process is primarily used in the coke oven industry. The Claus process initially had some problems associated with the excessive amounts of hydrogen cyanide, iron sulfide and iron cyanide present in the above concentrated acid gas stream. These problems have been resolved after special adjustments to the Claus unit.

The Wet Oxidative processes, mentioned earlier, are sulfur recovery processes in which elemental sulfur is the product. The Stretford process does not remove COS or other organic sulfur compounds from the gas stream.

The H_2S removal or sulfur recovery efficiency achievable for the processes in the coke oven industry are: Iron-Oxide process - 99 percent (for low gas volumes); Vacuum Carbonate process - 93 to 98 percent; Sulfiban process - 90 to 98 percent; Stretford process - 99.5+ percent; and the Claus Sulfur Recovery process - 95 to 96 percent.

Among the acid gas removal processes found in the coke oven industry, the amine and carbonate type solvent processes should have application in low-pressure gasification processes, or in treating low-pressure offgases from liquefaction processes. The two most common sulfur recovery processes in the coke oven industry are the Claus and Stretford processes. Both of these processes will have wide application in the coal conversion industry. The Claus is in service at a number of developing gasification processes, e.g., both the Hygas and Bigas pilot plants have Claus sulfur recovery units. The Stretford process is also in service at a number of coal conversion processes, e.g., Synthane pilot plant, Pittsburgh Energy Research Center, the SRC pilot plant at Fort Lewis, Washington, and the Sasol coal conversion plant in South Africa. Generally, the Stretford process is more economical when the acid gas stream contains less than 15 percent H_2S, whereas the Claus process is the economic choice for levels above 15 percent.

Consideration must be given to the interferences caused by high CO_2 and other impurities in the application of both the Claus and Stretford processes when used for coal conversion systems. CO_2 tends to neutralize the Stretford solution and reduces the absorption rate of the H_2S, thus necessitating higher rates of solvent circulation and larger units. High CO_2 affects the stability of the flame in the Claus reactor, and also results in higher COS concentrations in the tail gas from the Claus unit. Additional control of the tail gas from the Claus unit would be required before emission to the atmosphere. Other impurities also have undesirable effects on the Claus unit. For example, in the presence of ammonia, ammonium bicarbonate can form which reduces the performance of the Claus catalyst.

A comparison of the wastewater characteristics of the different processes are shown in Table 1-3. Although many similar constituents are present, their concentrations vary from process to process. The process wastewaters from the Byproduct coke plants contain large amounts of phenol, ammonia, sulfide, cyanide, and oil and grease. Various control technologies are being used to remove these pollutants.

Ammonia is being removed and recovered by steam stripping at alkaline pH, or by Phosam-W, a proprietary (U.S. Steel) process that uses scrubbing (ammonium phosphate solution) and distillation in combination to produce an anhydrous ammonia product. Sulfide removal from wastewater by steam stripping is not commonly practiced in the coke oven industry.

Phenols are being removed by solvent extraction, steam stripping and/or biological oxidation, and carbon adsorption. Biological treatment has been successful with coke oven wastewaters in meeting existing phenol regulatory limitation. Phenol removal efficiency of about 99.8 to 99.9 percent has been achieved by the activated sludge system: B.O.D. removal has ranged from 85 to 95 percent.

All the above coke oven wastewater treatment and byproduct recovery technologies should have application in coal conversion waste treatment. Except for the low pressure and high temperature gasification processes (e.g., K-T process), other gasification and all coal liquefaction processes appear to produce process wastewaters with similar pollutants and composition ranges (See Table 1-3). Therefore, coke oven technologies should be applicable to these processes for wastewater treatment.

TABLE 1-3. COMPARISON OF PROCESS WASTEWATERS

	Coke Plant[(1)] Ammonia Liquor mg/l	Synthane[(2)] mg/l	Lurgi[(3)] mg/l	Koppers-Totzek[(4)] mg/l	SRC-I mg/l
pH	8.4	8.6	8.9	8.9	8.0
Suspended Solids	4,000	600	5,000	50	300
Phenol	1,000	2,600	3,500	-	4,500
C.O.D.	10,000	15,000	12,500	70	15,000
Thiocyanate	1,000	152	-	-	-
Cyanide	50	-	-	0.7	-
Ammonia	5,000	8,100	11,200	25	5,600
Chloride	6,000	500	-	600	-
Carbonate	-	6,000	10,000	1,200	-
Sulfide	1,250	1,400	-	-	4,000

1) See other wastewater compositions in Section 4.
2) Illinois No. 6 Coal feed. Bibliography 26.
3) Lurgi Sasol plant wastewater.
4) Private communication with the Koppers Co., Inc., Pittsburgh, Pa.

Many coke oven plants recycle wastewaters containing high-cyanide concentration for coke quenching. Although alkaline chlorination of cyanide containing wastewaters is successfully practiced elsewhere in steel mills, it is not used for coke oven wastewaters because existing cyanide limitations for the coke oven industry are met without additional treatment. Quenching of ash and char with untreated wastewater may not be premitted for the coal conversion industry.

Some coke oven plants use a byproduct light oil upgrading process which has a potential application in the synfuels industry. This process, called the LITOL$^{(R)}$ process, has been developed and licensed by the Houdry Division of Air Products and Chemicals, Inc. It is a catalytic process by which coke oven light oils are refined and dealkylated to produce high quality, even reagent grade, benzene at essentially stoichiometric yields. The process has been used commercially since 1964, and is in use in the U.S. and several other countries.

The coke ovens are a major source of air pollution emissions in the steel industry. Topside coke oven workers have a substantially higher risk of lung cancer than the average worker, probably from carcinogenic materials associated with the particulate fraction of the coke oven emissions. Various schemes to control these emissions and alleviate potentially adverse health effects are being developed.

These include: coke oven equipment design changes; improved coke oven operating and maintenance techniques; collection of coke oven fugitive emissions; and control of coke oven fugitive emissions. Equipment design changes include such items as: adding another gas collection main on coke oven battery; hydraulically operated mechanical gooseneck cleaners; magnetic lid lifting equipment on larry car; screw feeders on all larry car discharge hoppers; modified steam aspiration nozzles; modification of stand-pipe caps; replacement of luted doors with knife-edge self sealing doors equipped with spring-loaded adjustable plungers to maintain design pressure on knife edges; and sealing of leveler door.

Improved coke oven operating and maintenance techniques include various innovative procedures designed to minimize fugitive emissions from openings and leaks associated with the charging, coking cycle, pushing/discharging and underfiring/heating operations. The collection of coke oven emissions include various hood and duct configurations which are custom designed to withstand high temperatures and to handle corrosive gases. Also, they must be able to offer the maximum collection efficiency with the least interference to the coke making operations.

The control of the fugitive emissions subsequent to collections has been successfully applied by use of the following air pollution control devices: high energy scrubbers, electrostatic precipitators and fabric filters. These devices have proven capable of capturing submicron particle size fractions of the smoke and particulate matter associated with coke oven fugitive emissions. Also, the devices are able to handle large volumes of corrosive gases containing condensed tar at their upper temperature limits (600 to 1,000°F). These fugitive emission control technologies will have application in the synfuels industry in analogous operations, e.g., in ash quenching, SRC solidification operations, and in the collection and control of the building exhausts and vents associated with coal conversion systems.

A summary list of the various coke oven control technologies that may have potential applications in the coal conversion industries is shown in Table 1-4.

A majority of the control technologies listed in Table 1-4 has been tested in coal conversion applications; however, most of these applications have been in process development unit or pilot scale coal gasification and liquefaction systems. A few successful uses have been with commercial first generation coal gasification processes, e.g. the Lurgi process. Applicability of the control technologies does not mean that the control technology can be duplicated (similar size equipment) from the coke oven design to the coal conversion application. In general, the composition, flow rate, temperature and pressure of the specific coal conversion system wastes will not be identical to the coke oven case; these differences, however, must be taken into consideration during the design of the control technology. Design information or scale up factors in comparison to coke oven application should be developed through laboratory or pilot scale testing with actual coal conversion wastes to determine the system design and to develop its costs.

TABLE 1-4. COKE PLANT CONTROL TECHNOLOGIES AND THEIR APPLICABILITY TO COAL CONVERSION

Coke Plant Control Technology	Applicability To Coal Conversion Systems
Acid Gas Treatment	
Amine solvents	Suitable for removal of H_2S and CO_2 from low pressure raw product and off gases. Solvent degradation may be encountered. High CO_2 level may produce a Claus feed with too low an H_2S concentration.
Carbonate solvents (e.g. Vacuum carbonate and Benfield)	Suitable for selective removal of H_2S and CO_2. Processes partially remove carbonyl sulfide and cyanides.
Sulfur Recovery	
Stretford	Suitable for low H_2S (less than 15%) containing gases. Organic sulfur not removed. High CO_2 levels require large units.
Claus	Applicable to high H_2S (greater than 15%) containing gases. Removal of high levels of cyanide, ammonia and hydrocarbons will be required.
Fugitive Emissions Control	
Enclosed coke pushing and quenching system	Potentially suitable for ash quenching, SRC solidification applications.
Fume recovery and scrubbing	Applicable to analogous sources
Improved operating Procedures and maintenance	Applicable to analogous sources
Byproduct Recovery/Refining	
Ammonia from wastewater (Stripping, Phosam - W)	Suitable for sour waters.
Ammonia from raw gases (Scrubbing, Phosam - W)	Applicable to low pressure gas purification.

TABLE 1-4 (Continued)

Coke Plant Control Technology	Applicability To Coal Conversion Systems
(Byproduct Recovery/Refining Continued)	
Phenol from wastewater (Solvent extraction)	Suitable for process wastewater containing 1,000 mg/l or more phenol.
Tar, naphthalene, light oil from raw gases	Suitable, but design must be modified for different pressures, temperatures and compositions.
Light oil refining (e.g. Litol process and solvent extraction)	Suitable for recovery of BTX from coal derived naphthas.
Wastewater Treatment Technology	
Biological oxidation; carbon adsorption; ammonia, phenol and oil removal processes	Generally applicable: design basis must be established for the specific waste.

An assessment of the health effects of coke oven emissions was recently made by EPA (Office of R&D) and a draft report was issued in April, 1978. The summary findings of the above report are as follows:

- Exposure to coke oven emissions provides an elevated risk for cancer of all sites and non-malignant respiratory diseases to coke oven workers and an increased risk among lightly exposed workers (non-oven workers in coke plant).
- The general population, which includes the young, the old and the infirm in the vicinity of a coke oven plant should be considered more susceptible than the workers, especially for development of chronic bronchitis, since they are generally in poorer health.
- Coke oven emissions contain an array of identified carcinogens, irritants, particulate matter, trace elements, and other chemicals. The toxic effects observed in both humans and animals are greater than the effects that can be attributed to any individual component. Thus "coke oven emissions" as a whole should be considered the toxic agents.
- There is an exposure difference of about 2 orders of magnitude estimated between lightly exposed workers and people living in the vicinity of a coke plant. Since these lightly exposed workers show an elevated risk for cancer and non-malignant respiratory disease, it is reasonable to assume that levels up to one-hundreth of those to which lightly exposed workers are subjected could cause an increased risk to the general population.

Since the coke oven and the coal conversion system emissions have many of the same hazardous components in high concentrations, such as H_2S, CO, CO_2, hydrocarbons and polynuclear aromatics, there is a potential occupational health hazard to coal conversion plant workers and the general population in the vicinity of the plant. Many of the new control technologies under development in the coke oven industry, especially those for fugitive emissions control, should result in significant removal of these hazardous pollutants. Whether or not additional controls will be required cannot be defined yet, since these new technologies have not been in use for a sufficiently long period of time.

SECTION 2

INTRODUCTION

In the primary contract with the U.S. Environmental Protection Agency, Catalytic, Inc. has been directed to conduct a program aimed at: assessment of pollution control needs, determination of available control technologies, and development of new control technologies for the products and byproducts of coal conversion (coal gasification and liquefaction) systems. Whereas there appeared to be gross similarities between the products, byproducts and waste-streams from the coal conversion and coke oven industry, and whereas the application of coke oven controls to the coal conversion industry appeared to be transferable, one of the assigned tasks (Task No. 10) in the project has been to determine the potential applicability of coke oven control technologies to the coal gasification/liquefaction industry.

The coke oven industry is long established and employs many types of air and water pollution control equipment. This industry has been active in the development of new environmental control technologies, especially for fugitive emission control, desulfurization and process wastewater treatment. The objective of the Catalytic study has been to review the coke oven control technologies and identify those that would have application to coal conversion process/waste streams. The approach methodology has been to characterize (compositions and quantities) those coke oven process and waste streams which have counterparts in coal conversion processes, and to identify and review the control technologies that could be applied to the coal conversion industry.

A meeting and discussions were held with representatives of the American Iron and Steel Institute (A.I.S.I.) and the American Association of Coal and Coke Fuel Dealers to obtain technical data.

A plant visit was made and consultations were held with representatives of an operating coke plant for first hand observations and discussions of the applications of processes and control technologies. To supplement discussions with E.P.A., A.I.S.I. and others, a comprehensive literature review was conducted utilizing computer-based technical literature search services to obtain published information on environmental controls and processes relating to coke oven systems byproducts. From the approximately 250 technical articles and text abstracts retrieved, a large number of publications were found to have significant information pertinent to the study.

Existing and proposed State and Federal regulations concerning disposal and treatment of waste materials were reviewed and are included in this report.

A brief assessment of health effects attributed to coke oven emissions, based principally on information released in draft form by the EPA's Office of Research and Development, is also part of this report.

A material balance for a typical coke plant was prepared. The balance embraces all the major unit operations and provides approximate compositions and quantities of the major process and waste streams. Both literature references and engineering judgment were applied in developing this information.

Comparisons of the waste characteristics from coke ovens with selected coal gasification and liquefaction process wastes have been made and recommendations offered regarding the control technologies for air, water and solid wastes that could be appropriately applied to coal conversion processes, including discussions on the conditions of applicability.

Results of an extensive review of coke oven control technology have been reported with special emphasis on coke oven gas desulfurization and wastewater treatment control strategies. Capital and operating cost data for these control strategies and some major process unit operations are included, whenever available.

SECTION 3

DESCRIPTION OF COKE OVEN PROCESSES

Coke is made from the destructive distillation of coal in an oven or retort in the absence of air; a process also referred to as pyrolysis or, more frequently as carbonization. Coke is the solid carbonaceous residue remaining after the high-temperature distillation of moisture and volatile matter from the coal. It is used primarily in blast furnaces, in foundries and in gas producers. Approximately 16 percent of the bituminous coal mined in the United States is converted to coke.

The coal used in coke making is usually a blend of high-volatile coal with 10 to 50 percent low-volatile coal. In order for the coal to form a strong, coherent coke, expansion is restrained in the oven during the heating process. Also, the coal should not contain more than 1.5 percent sulfur or 9 percent ash. Bituminous coal is the most suitable type because it has the best agglomerating properties.

Besides coal types, other important variables that affect coke and byproducts characteristics are oven temperature, residence time and oven construction features. For example, the effect of carbonizing temperature on the yields of coke and byproducts are shown in Figure 3-1. Although a small amount of coke has been made in the United States by low-temperature (450 to 700°C) and medium-temperature (700 to 900°C) carbonization, most of the coke is produced by high-temperature carbonization at 1,000 to 1,150°C.

There are two proven high-temperature processes: "Byproduct" coke oven (recovery type) and "Beehive" (nonrecovery) processes. Approximately 98 percent of the total coke production in the United States is from Byproduct coke plants. Therefore, the major focus of this report will be on the Byproduct coke oven process, with only brief discussions of the Beehive and low-temperature processes.

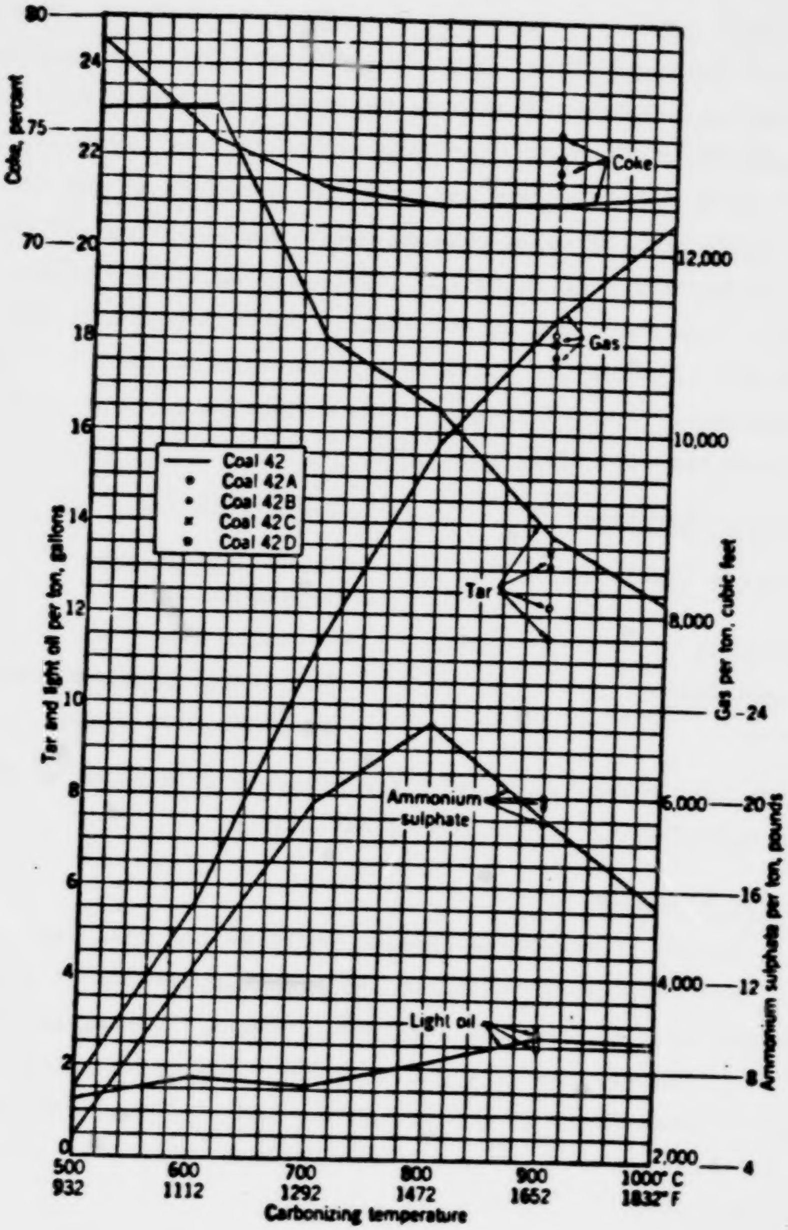


Figure 3-1. Yields of carbonization products from Upper Banner seam coal(43).

BYPRODUCT COKE OVEN PROCESS

The Byproduct process is oriented toward the recovery of the gaseous and liquid chemicals produced during the coking cycle. The principal unit of equipment in the manufacture of coke is the coke oven, which is a narrow chamber, usually about 38 to 50 feet long, 13 to 16 feet high, and tapering in width from 17 to 20 inches at one end to 15 to 16 inches at the other. A typical oven holds from 16 to 24 tons of coal, and the ovens are usually built and operated in batteries of 10 to 100 (typically 80 to 100) ovens. Although coke production from each oven is basically a batch process, a coke oven plant uses this battery of ovens for continuous production of coke oven gas and byproduct chemicals. Some of the major high-temperature coke oven processes with their characteristic differences are:

Process/Developer	Description
Koppers (Includes Becker)	Cross-regenerative byproduct oven
Wilputte	Vertical flue oven
Semet-Solvay	Horizontal heating flues
Otto	Vertical flue ovens

The batch coke making step and the continuous processing of the raw coke oven gas are described in the following paragraphs.

General Process Features

Coal is charged to the ovens through ports in the top, which are then sealed. The heat required to maintain the high temperature is supplied to the ovens by burning some of the coke oven gas produced. Coking is largely accomplished at temperatures of 1,090 to 1,150°C and at atmospheric pressure for a period of about 16 to 27 hours. At the end of the coking period, the coke is pushed from the oven by a ram and quenched with water in an area remote from the ovens.

The gaseous mixture generated in the Byproduct coke oven is composed of permanent gases which form the final purified coke oven gas for the market, accompanied by condensable water vapor, tar, light oils, solid particles of coal dust, and heavy aromatic hydrocarbons. Figure 3-1 shows the yields of coke oven byproducts at various carbonizing temperatures for a given coal type. The raw gas also contains pollutants such as ammonia, hydrogen cyanide, cyanogen, hydrogen sulfide, carbonyl sulfide and carbon disulfide. Since raw gas from coal gasification processes and off-gas from coal liquefaction processes contain chemicals and pollutants similar to those listed for the raw Byproduct coke oven gas, it is of significant importance to this study to place particular emphasis on the processing schemes used to remove, recover or destroy these chemicals and pollutants.

Figure 3-2 is a process block flow diagram of a typical byproduct coke oven plant. It shows the various processing schemes used to recover chemicals and remove pollutants from the raw coke oven gas. The sequence of the unit operations can be varied; however, the following process sequence for the manufacture of coke and its major byproducts is typical:

1. Coal is transferred, crushed, and screened.
2. Coal is charged to a hot empty oven.
3. Coal is chemically transformed to coke and volatiles by pyrolysis.
4. Hot coke is pushed out of the oven, quenched, and transported for storage and use.
5. Some condensable products (primarily tar and ammonia) are condensed and collected in the hydraulic main and primary cooler. Tar and excess ammonia liquor are recovered.
6. Coke oven gas is pulled through an exhauster with a suction of 15 to 20 inches of water and is discharged at a pressure of 45 to 75 inches of water.
7. The coke oven gas then passes through electrostatic precipitators which remove most of the remaining traces of tar.
8. Ammonia is removed from the gas as ammonium sulfate, or as anhydrous ammonia.
9. The gas is further cooled and light ends are removed by absorption in a petroleum-based absorbent (e.g., No. 2 fuel oil, straw oil). Some plants have the facilities to upgrade or refine the light oil and recover benzene, toluene and xylene (BTX).
10. Hydrogen sulfide is removed from the coke oven gas using various processes (see Section 4).
11. Clean coke oven gas is metered and sent to users.

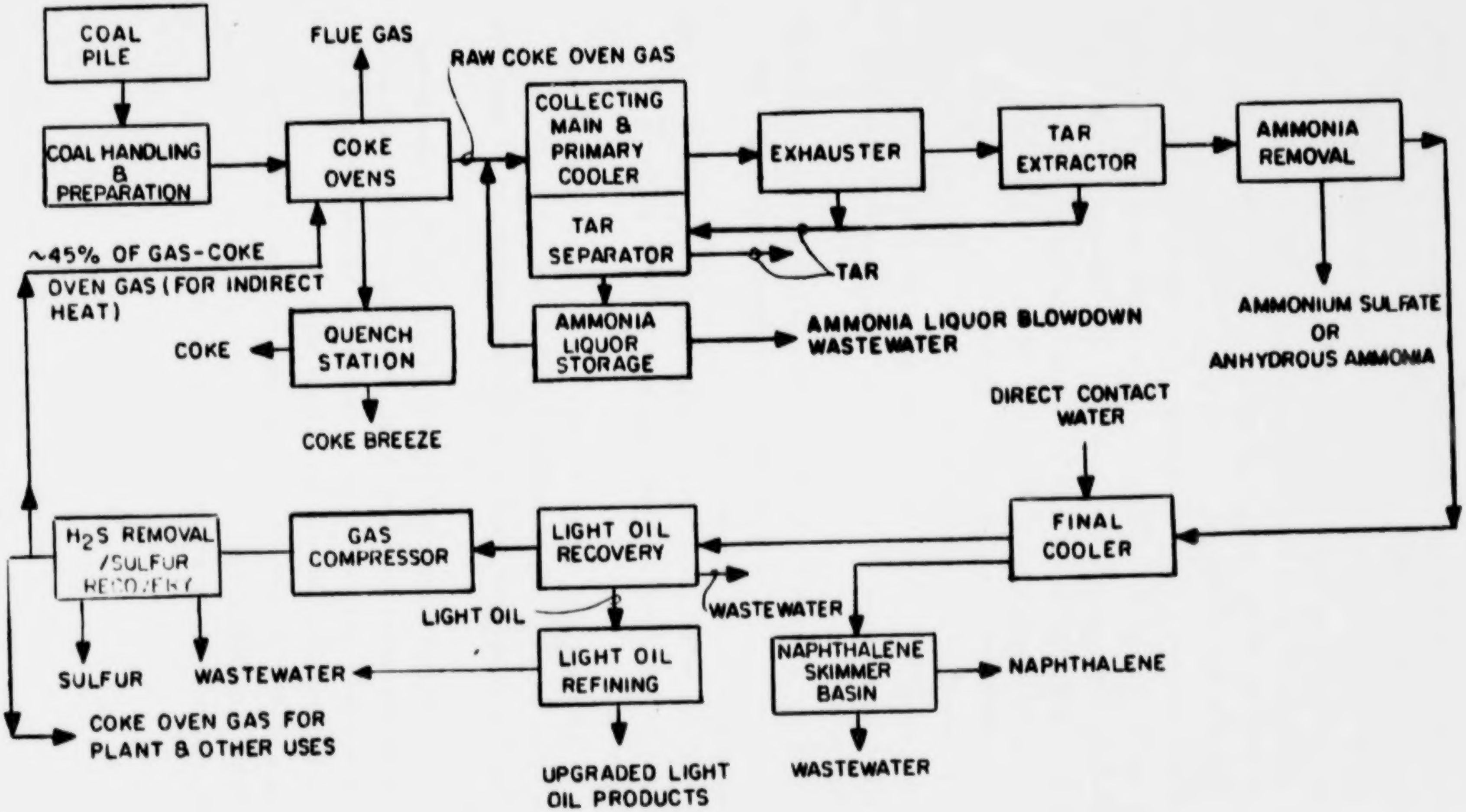

COAL PILE
COAL HANDLING & PREPARATION
COKE OVENS
FLUE GAS
RAW COKE OVEN GAS
COLLECTING MAIN & PRIMARY COOLER
TAR SEPARATOR
EXHAUSTER
TAR EXTRACTOR
AMMONIA REMOVAL
TAR
AMMONIUM SULFATE OR ANHYDROUS AMMONIA
~45% OF GAS-COKE OVEN GAS (FOR INDIRECT HEAT)
QUENCH STATION
COKE
COKE BREEZE
AMMONIA LIQUOR STORAGE
AMMONIA LIQUOR BLOWDOWN WASTEWATER
DIRECT CONTACT WATER
FINAL COOLER
H_2S REMOVAL /SULFUR RECOVERY
GAS COMPRESSOR
LIGHT OIL RECOVERY
LIGHT OIL
WASTEWATER
NAPHTHALENE SKIMMER BASIN
NAPHTHALENE
SULFUR
WASTEWATER
LIGHT OIL REFINING
COKE OVEN GAS FOR PLANT & OTHER USES
UPGRADED LIGHT OIL PRODUCTS
WASTEWATER

Figure 3-2. Simplified block flow diagram of a byproduct coke oven plant.

Detailed descriptions of the foregoing operations and processes are presented in the following paragraphs.

Coal Handling and Preparation

The primary functions are to prepare coal by blending, crushing mixing, and pulverizing it to the required size and to transport the prepared coal to the ovens for coking. A typical analysis of a mixed coal charge would be as follows:

	Percent (by wt.)
Volatile Matter	30.00
Fixed Carbon	63.65
Ash	5.50
Sulfur	0.85
	100.00

As mentioned previously, a blend of high-volatile bituminous coal with 10 to 50 percent of low-volatile bituminous coal is used to obtain a composition similar to the above analysis.

After blending, the coal is crushed until it passes through 2-inch openings, and is then pulverized in a hammer mill so that about 80 percent passes through a 1/8-inch screen. In the hammer mills, approximately 0.1 gallon of oil per ton of coal is added to control the bulk density of the coal which is then ready for charging to the coke oven.

Coke Oven Operation

The coal is delivered to the ovens by means of charging cars (larry cars) that transport a measured amount of coal from the storage bins. This coal is introduced into the ovens through charging holes at the top. The ovens are heated by either raw or purified coke oven gas, which burns in vertical heating flues set in the side walls of the ovens. Air for combustion is drawn through regenerators which cool the flue gases to about 750°F before entering the stack. About 40 to 45 percent of the total coke oven gas produced is used to supply heat for the ovens.

When the coal is charged into a hot oven, the layer of coal adjacent to the heated walls is quickly decomposed. A plastic layer is formed, and moves slowly toward the center of the oven as carbonization proceeds. Coal is an extremely poor conductor of heat and the center of the charge remains at a low temperature for several hours. The average coking rate is about 1 in/hr (1/2 in/hr from each side) and it takes about 16 hours to complete the coking cycle. At the end of the cycle, the coke is pushed out of the oven into a quench car. The hot coke is quenched by a water spray, and is then dumped onto an inclined coke wharf where it dries and cools.

Recovery of Tar and Ammonia liquor

The volatile matter and gas evolved during the coking process (raw coke oven gas) leave the ovens through standpipes (vents) and pass into a gas collecting main. There, the temperature of the gas is reduced from a range of approximately 800 to 1,300°F to about 175 to 200°F by spraying it with recycled ammonia liquor. This reduction in gas temperature causes condensation of approximately 75 percent of the tar in the gas and most of the water vapor in the raw gas.

From the collecting main, the gas passes to the primary coolers, where it is cooled to about 85 to 104°F by ammonia liquor spray. This cooling removes additional tar and water vapor and, again, a small portion of the total ammonia in the gas. The gas is next conducted to an exhauster (positive-displacement type). Beside compressing the gas, it also serves to remove tar by the high-speed swirling motion imparted to the gas.

The gas passing through the exhausters still contains traces of tar fog, which is further reduced by electrostatic precipitators (ESP). The tar drains from the bottom of the precipitators into a settling pit, which also collects the tar removed in the collecting main and primary coolers. It is then pumped from the pit and transferred to a storage tank, where water is decanted. This tar, containing approximately 2 to 5 percent moisture, is sold for processing and recovery of valuable aromatic compounds such as food coloring.

The condensed water, which results from gas cooling in the collecting main and primary coolers, appears as excess ammonia liquor and is the major process wastewater from the Byproduct coke oven plant. This stream is also referred to as ammonia liquor blowdown. The excess ammonia liquor is treated before discharge for byproduct recovery and pollutant removal according to the various schemes discussed in Section 7.

The coke oven gas which has passed through the tar extractors (ESP) is next sent to the ammonia removal unit for recovery of ammonia by one of the following methods:

1. Indirect process. The ammonia is removed from the gas by scrubbing with water. Scrubber blowdown is treated by an alkali solution and steam stripping; the stripped vapor is then passed through a saturator containing a solution of sulfuric acid to recover ammonium sulfate.
2. Direct process. Raw coke oven gas, after separation of tar, is passed through a saturator containing a solution of sulfuric acid to remove ammonia.
3. Semi-direct process. The ammonia in the liquor, which is produced by direct and indirect cooling, is removed by alkali treatment and distillation, and added to the gas stream. This stream is then passed through an absorber (saturator) containing dilute sulfuric acid to extract the ammonia as ammonium sulfate.

Of these three processes, the semi-direct, developed by Koppers, is most extensively used in the U.S. (Note: A new process known as Phosam-W (U.S. Steel) is emerging. This provides for ammonia removal by scrubbing the gas with a lean ammonium phosphate solution and then recovering anhydrous ammonia from the scrubbed liquid by stripping and distillation. See further discussion of this process in Section 7.0).

After the ammonia removal unit, the gas passes through the final coolers where direct contact water is used to cool the gas to a temperature of 70 to 90°F. A major portion of the naphthalene condenses out of the gas as a result of this cooling and is recovered from the cooling water at the settling basin or in flotation cells where it is skimmed off as it rises to the top. The naphthalene is either added to the tar or is processed further to produce a commercial product. In some facilities, it is recovered from the cooling water by having tar circulate countercurrently to the flow of water in the base of the final cooler.

For the recovery of light oil, which is generally the last step in the coal chemical recovery process, there are three general methods used:

1. Refrigeration and compression involving temperatures below minus 70°C and pressures of 10 atmospheres.

2. Adsorption by activated carbon followed by heating to recover organic compounds.
3. Absorption by solvents involving washing of the gas with a petroleum solvent, coal-tar fraction, or other absorbent, followed by steam distillation of the enriched absorbent to recover the light oil.

Light Oil Refining

The traditional method for purifying the recovered light oil is to wash it with sulfuric acid and caustic soda, followed by distillation to separate benzene, toluene, xylene (BTX), and solvent naphtha cuts. The thiophene content of benzene produced by acid washing is high (100 to 400 ppm) and precludes utilization of this benzene in many chemical reactions, particularly where sulfur sensitive catalysts are employed. As a result, coke oven BTX has a less marketable demand than petroleum derived benzene, which contains less than 1 ppm thiophene.

The Houdry LITOL process was developed to purify the light aromatic fraction produced as a byproduct of high-purity BTX and is also capable of dealkylating the toluene and xylene to benzene at high selectivities, whenever desired. Nonaromatic materials (mainly paraffins, olefins, diolefins, naphthenes, and sulfur compounds) are completely converted to lighter hydrocarbons and to hydrogen sulfide.

Figure 3-3 shows a simplified block flow diagram for the LITOL process. Applicability of the LITOL process to coal conversion systems is discussed in Section 7 under Light Oil Upgrading Processes.

Desulfurization of Coke Oven Gas

The gas, after being stripped of its ammonia and light oil, is next sent to the desulfurization unit for sulfur removal. Many processes available for gas purification are discussed in detail in Section 7. Historically, the dry oxidative process using iron oxide boxes has been the most extensively used method for sulfur removal. However, the Vacuum Carbonate, the Holmes-Stretford, and more recently, the Sulfiban process have moved into commercial prominence.

After the gas is desulfurized, it is ready for use as a clean fuel.

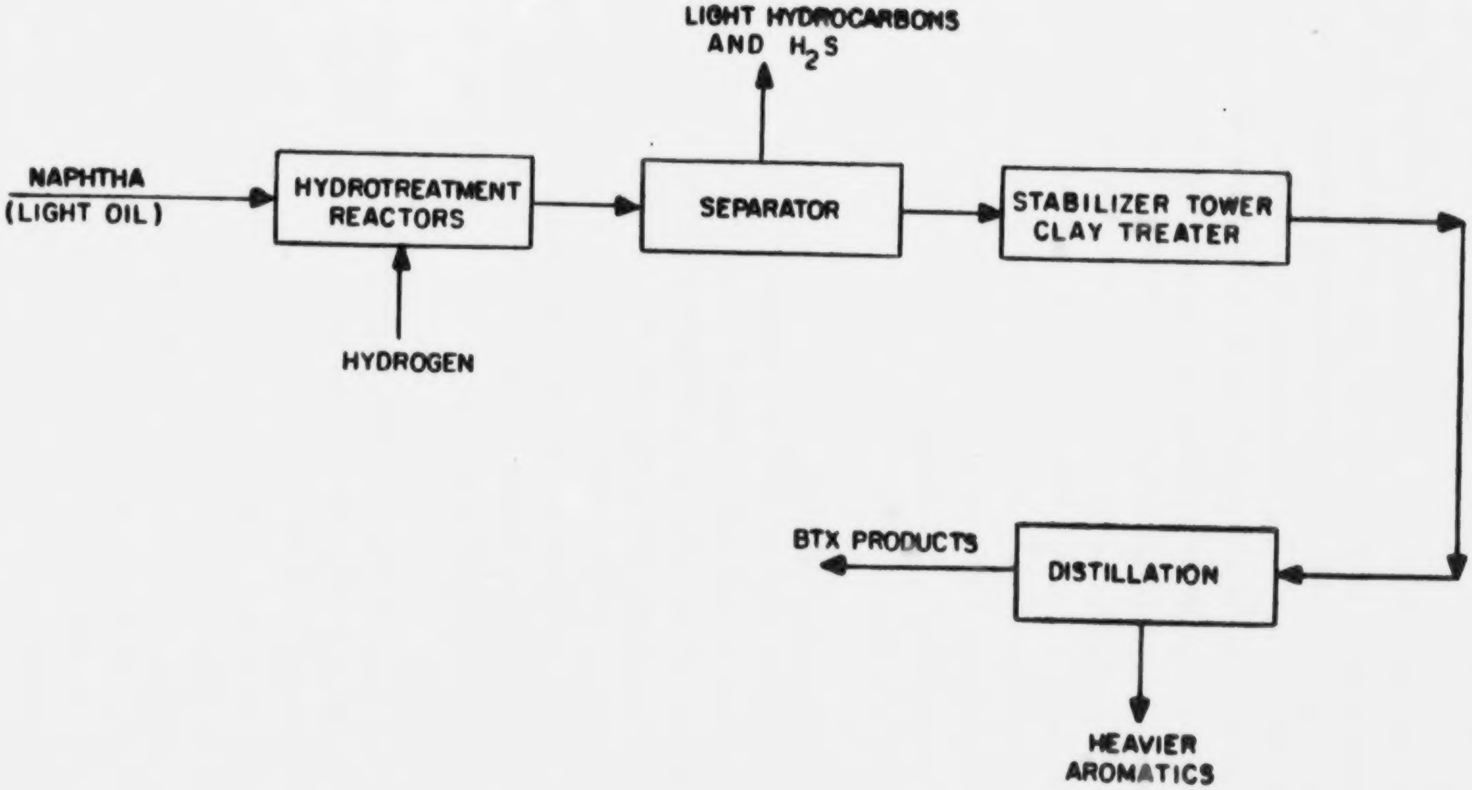

NAPHTHA
(LIGHT OIL)
HYDROTREATMENT REACTORS
HYDROGEN
SEPARATOR
LIGHT HYDROCARBONS AND H_2S
STABILIZER TOWER CLAY TREATER
DISTILLATION
BTX PRODUCTS
HEAVIER AROMATICS

Figure 3-3. Simplified block flow diagram of the Houdry LITOL Process.

OTHER COKE OVEN AND RELATED PROCESSES

Beehive Process

Except for the coke, this is a nonrecovery type of process. The Beehive oven is a refractory-lined enclosure with a dome-shaped roof. The coal charge (10 to 15 tons), deposited onto the floor of the oven through a trunnel head in the roof, is leveled to give a uniform depth of material. Openings above a door on the side of the oven are restricted to control the amount of air reaching the coal. This air is required to burn the volatile products distilled from the coal and thus generate heat for further distillation. The carbonization process begins at the top of the coal pile and works down through it. The volatile matter being distilled burns near the top of the oven and the combustion products leave through the opening in the roof. Upon completion of the coking (which takes from 48 to 96 hours), the coke is "watered out" or quenched. After quenching, the coke is "drawn," i.e., removed either mechanically and/or by hand.

Low Temperature and Recent Processes

There are numerous types of process equipment used and byproducts generated from the low-temperature processes. Most of these processes are commercially prominent in Europe for the production of domestic fuels, along with gas and chemical byproducts. Table 3-1 summarizes some old commercially developed low-temperature carbonization processes.

The only commercially successful, low-temperature (570°C) carbonization process ever utilized in the United States was the "Disco" process. However, because of the availability of other cheaper fuels, the company discontinued the process in 1963.

In the Disco process, wet fine coal from the washery goes through five basic steps: predrying; roasting; carbonizing in the retorts; cooling the char; and screening and loading.

The process is unique because it produces a final semicoke or lump char directly from the fine coal in indirectly heated continuous rotating retorts. This is done, without a briquetting step, through preliminary oxidation or "roasting" of the coal in contact with air, thus destroying a portion of its excessive caking characteristics. In the rotating retort, the oxidized coal, together with recycled char, rolls up into balls of char without adhering to the sides of the retort. The balls of char are screened and sold as smokeless domestic product.

TABLE 3-1. OTHER COKE OVEN AND RELATED PROCESSES

Process	Status	Objective	Process Description	Distribution of Contaminants in Products
Disco	Was installed by Disco Co. near Pittsburgh in the 50s.	Coke, tar and gas.	Designed for certain coals. Bituminous coal, ground to 3/8-in size, is heated in a revolving steel retort. The carbonizer gas is at 450-480^{o}C.	The low temperature of operation does not remove any contaminants. Feed coal has 2.2% S, and coke produced has 2.1% S.
Hayes Process	Was operated by Allis-Chambers Moundsville, W.V. in the 50s.	Coke, tar and gas.	Uses a rotating tube retort with a screw conveyor. The temperature at feed end is 595-705^{o}C. The gas has a heating value of 939 Btu/ft^{3}.	Coke contains 3.5% ash compared to 9.85% for coal.
Krupp-Lurgi Process	Developed in the 30s. Only large scale plant is in Germany.	Coke, tar and gas.	Oven consists of six carbonization cells; entering gas is at 620^{o}C and exit gas at 570-580^{o}C.	The ash content of coke is 3.8% versus 5.4% for coal. The gas contains 6% nitrogen.
Brennstoff-Technak Cellon Jones Oven Carmaux Oven Otto Retort Weber Process Phurnacite Process Parker Retort	Process developed for specific coals, e.g., slightly caking.	Coke	Fixed-bed operation is used.	The temperatures control contaminant removal from the coke.
Rexco Process	Developed and operated in England.	Coke, tar and gas	The directly heated fixed-bed retorts are operated at 700^{o}C.	Rexco coke has 7.2% ash versus 4.9% for coal.

TABLE 3-1. (Continued)

Process	Status	Objective	Process Description	Distribution of Contaminants in Products
Koppers	Developed in Germany.	Coke, tar and gas	Uses a continuous vertical retort for non-caking coals. Temperatures of 800-1,000°C are attained.	Higher temperatures would remove S, N and trace metal contaminants from the coke.
Parry Process	Developed by U.S. Bureau of Mines	Coke, tar and gas	Uses entrained carbonization; temperatures are 1,038°C.	Fine particle size of Feed coal and high operating temperatures remove S, N and trace elements from the coke.

The byproduct gas generated during carbonization is cooled, scrubbed, and returned to the retort furnace to provide heat for carbonization. Low-temperature tar is recovered and sold for further processing.

Recent Processes--

In order to find solutions to our energy problem, several new coal carbonization/pyrolysis processes are in the developmental stage. They produce more liquids and gas products than the Byproduct coke oven process. Table 3-2 briefly describes these new processes. Additional characteristics of the important processes are given in Sections 5 and 6.

There are no commercial low temperature coke oven processes available in the U.S. today. However, low temperature carbonization of the char and filter cake residue of some coal liquefaction processes such as the SRC-I process is being considered for recovery of carbon values. (Note: The SRC-I process is discussed in further detail under Section 6 of the report.)

FMC Corp. operates a demonstration plant (265 TPD) in Kemmerer, Wyoming which produces a coke from sub-bituminous, and non-coking local Wyoming coals. The FMC coke process is a continuous process unlike the coke oven battery which is a cyclical batch operation. The process consists of a pyrolysis section where coal is devolatilized in a sequential series of fluid beds operating under controlled time, temperature and environmental conditions. It also has a coke forming section consisting of briquetting, curing and coking. The coke product is not exposed to the atmosphere until it appears as cooled product being delivered to the storage silo. There are no pushing, charging, door, topside or quenching emissions as associated with the byproduct coke ovens. Emissions which do occur are from the coal preparation section and the three vessels in the fluid processing section. These emissions are incinerated in a front end afterburner, emissions from briquetting are also controlled by the front end afterburner after passing through cyclonic separators. Emissions from the fluid bed primary and secondary coolers are combined and passed through a single baghouse. The organic emissions from the curing oven and kiln are oxidized in a back end afterburner. Fugitive emissions from kiln air locks, coke cooling, coke loading and associated transfer points are controlled by a baghouse. No commercial plant has been built based on this process.

TABLE 3-2. RECENT COAL CARBONIZATION/PYROLYSIS PROCESSES

Process	Status	Objective	Process Description	Distribution of Contaminants in Products
Char Oil Energy Development (COED)	Developed by FMC, Princeton, NJ in 1962: 36 tons/day pilot plant. COED/Cogas process has been selected for demonstration.	Maximize liquid production from coal by pyrolysis.	Uses multi-stage fluidized-bed pyrolysis of coal. Catalytic hydrotreating of the oil yields synthetic crude suitable as petroleum refinery feedstock. The product gas can be used as boiler fuel or for gasification. Four fluidized beds have temperatures from 316-816^{o}C; char 59.5%, oil 19.3%, gas 15.1%, liquor 6.1%, based on Illinois No. 6 coal.	The low temperature of pyrolysis will concentrate the trace elements and N, S compounds in the char. The liquid product contains S, N which are removed by hydrotreatment.
COALCON (Hydrocarbonization)	Developed by Union Carbide: pilot plant in South Charleston	Produces liquid and gas	Sized, dried and preheated coal is fed to a dry, fluidized-bed hydrogenation is gasified.	First state hydrogenation would remove S, N to some extent depending on
Clean Coke	Developed by U.S. Steel 1972 500 lb/day (Process Development Unit)		Detailed designs of PDU's on: (1) Coal and coke preparation, (2) Carbonization, (3) Hydrogenation, (4) Slurry oil preparation, and (5) Binder preparation. Coal after beneficiation is split into two fractions. Portion of coal carbonized and desulfurized to produce metallurgical coke. The rest of coal is slurried with process derived oil and hydrogenated.	The liquid produced is desulfurized by hydrogen treatment. The char contains 0.5% S versus 1.74% for coal.

TABLE 3-2. (Continued)

Process	Status	Objective	Process Description	Distribution of Contaminants in Products
Cogas	Developed by Cogas Develop Co., Princeton, 2.5 TPD and 50 TPD pilot plants are being operated. COED/Cogas has been selected for demonstration.		Variation of COED process; Gasifier-Combuster operates at 816-927^{o}C. Med-Btu gas is cleaned of S.	The liquid is desulfurized by hydrogen treatment.
Garrett's Coal Pyrolysis	Developed by Occidental Petroleum Corp. 3.6 TPD pilot plant is being tested.		Crushed coal is introduced into the pyrolyzer in a stream of recycle gas and is pyrolyzed at 593^{o}C through contact with hot char (649-841^{o}C). Part of product gas is reformed for hydrogen to hydrotreat tar. Yields are: char 56.7%, tar 35%, gas 6.5%, and 1.8% water.	Desulfurization of char by acid treatment is proposed. The trace elements will concentrate in the char.
Fractional Carbonization of coal.	Eddinger, R.T., et al. U.S. Patent 3,574,065	Liquids and gas	Staged pyrolysis and final combustion is used.	Fate of trace elements is the same as in any carbonization study.
Pyrolyzing of solid or liquid fuel.	A.M. Squires; U.S. Patent 3,597,327 8/31/71	Gas and char	Uses a two-stage fluidized-bed pyrolyzer. The heat is supplied to the lower zone by conduction from the top zone. The lower bed carbonizer is at 760^{o}C and the top one at 949^{o}C. Dolmite is used to remove the sulfur.	Fuel gas and coke products free of sulfur are produced. The fate of trace elements is not mentioned. (It is postulated that they would end up in the coke pellets.)

Pennsylvania Control Technology, Inc. has developed a prototype non-recovery type coking process which claims to minimize pollutant emissions. The unit presently operating at the Alverton Fuel Co., Alverton, Pa. essentially consists of two ovens with a single flue heating system. The hot gas from the combustion of the coal is mixed with fuel oil and air and burned in an incinerator situated between the ovens. The heat is recovered from the incinerator and is used for heating the flue system. The coking cycle lasts from 40-48 hours. The system is under 0.95 inches of water vacuum with outside air drawn through the trunnel head (coal charge points) on top of the ovens. The coke is removed from the ovens into an enclosed quench wharf and the gases are exhausted and burned in the incinerator. Tests conducted on emissions from this unit show 0.052 grains per standard cubic foot of air of particulate matter and 252 ppm of sulfur dioxide burning 0.7 percent sulfur coal. The test unit has been approved by the state regulatory agency, and four commercial development units at mine-mouth locations are in the planning stage.

SECTION 4

MATERIAL BALANCE AND WASTE CHARACTERISTICS OF COKE OVEN PROCESSES

BYPRODUCT COKE OVEN PROCESS

Typical Product/Byproduct Quantities

The quantity and characteristics of the coke product and chemical byproducts vary with coal types, oven temperatures, and operating conditions. Using the coal composition and operating conditions specified in Section 3 under "Coal Handling and Preparation," literature information shows that one ton of coal (wet and as fed to the oven) will yield 1,935 pounds of products and byproducts with the following typical slate:

	Pounds		Pounds
Coke	1,430	Ammonia, anhydrous	5
Coke Breeze	93	Light Oil (2.81 gal)	20
Tar (8.41 gal)	78	Gas (10,350 scf)	309

The remainder (65 lb) is assumed to be composed of condensed moisture and pollutants (e.g., particulates, phenolics) in the process wastewater and in the fugitive air emissions. The foregoing assumption needs verification, since literature data were not definitive regarding these losses.

The following summary of clean coke-oven gas composition is typical:

Constituent	Volume %	
	Typical	Ranges
CO_2	2.5	1.3 - 2.5
C_nH_m	3.5	3.1 - 4.0
CO	8.0	4.5 - 9.0
H_2	53.5	46.5 - 57.9
C_2 and homologs	30.0	26.7 - 34.0
N_2	2.0	1.5 - 9.6
O_2	0.5	0.2 - 0.9

Table 4-1, a detailed breakdown of the feed coal into various products, byproducts and contaminants, shows that the feed coal contains about 1.0 percent sulfur; and the product coke contains about 0.96 percent sulfur. The balance of the sulfur converts principally to hydrogen sulfide, carbonyl sulfide and carbon disulfide in the raw coke-oven gas.

Waste Characteristics

Process Wastewater--

The principal sources of byproduct coke plant process wastewater before treatment are ammonia liquor blowdown, final cooler blowdown water, light oil plant wastewater: 25 gallons, 25 gallons, and 30 gallons, respectively, per ton of coke for the plant utilizing the best available technology (BAT). Barometric condenser water is also a potential source when a crystallizer is used for ammonium sulfate production.

Table 4-2 presents typical pollutant concentrations in the ammonia liquor blowdown. The blowdown rates range from 18 to 90 gallons per ton of coal (dry basis) depending on the type of process used to remove ammonia from the coke oven gas. The Phosam-W and sulfuric acid scrubbing processes exhibit lower flows; higher flows occur with the outdated water scrubbing process.

Final cooler blowdown water represents the condensate resulting from cooling the saturated gas with direct contact cooling water. Typical pollutant concentrations in the blowdown are shown in Table 4-3. The quantity of condensed water ranges between 5 to 10 gallons per ton of coal (dry) and is one of the major sources of hydrogen cyanide in wastewater.

Table 4-4 shows representative pollutant concentrations in the light oil plant (also called benzol plant) wastewater. The volume of water generated from these sources ranges from 18 to 56 gallons per ton of coal (dry).

Plants with a crystallizer for ammonium sulfate production generally use barometric condensers that create large amounts of wastewater, ranging from 175 to 300 gallons per ton of coal (dry). Pollutant concentrations representative of barometric condenser water are:

Constituent	mg/l
Ammonia	20
Phenol	40
Cyanide	40
Oil	20

TABLE 4-1. YIELDS AND ANALYSES OF PRODUCTS OF BY-PRODUCT COKE OVEN PROCESS (SOURCE - BIBLOGRAPHY 51)

Product	Constituent	Percent of coal by weight	Analysis percent of product by weight
Coke	Ash	7.210	10.24
	Carbon	61.711	87.76
	Hydrogen	0.469	0.66
	Sulfur	0.683	0.96
	Nitrogen	0.270	0.38
	Totals	70.343	100.00
Gas	CO_2	1.042	6.66
	CO	3.154	20.14
	CH_4	7.468	47.69
	C_2H_4	1.529	9.76
	N_2	0.385	2.46
	H_2	1.366	8.72
	O_2	0.717	4.57
	Totals	15.661	100.00
Ammonia	Hydrogen	0.040	17.9
	Nitrogen	0.183	82.1
	Totals	0.223	100.0
Tar	Carbon	4.687	86.0
	Hydrogen	0.327	6.0
	Oxygen	0.436	8.0
	Totals	5.450	100.0
Liquor	Water	6.78	99.63
	Organics (phenolics)	0.025	0.37
	Totals	6.805	100.0
Light Oils	C_6H_6 (Equivalent)	1.102	100.0
Cyanogen	C_2N_2	0.078	100.0
Carbon disufide	CS_2	0.013	100.0
Hydrogen sulfide	H_2S	0.325	100.0
		100.00	

TABLE 4-2. AMMONIA LIQUOR BLOW-DOWN COMPOSITION
(SOURCE: BIBLIOGRAPHY 7)

Constituents	Concentration Range
Total ammonia, mg/l as N	3,000 - 9,000
Free ammonia (% of total)	20 - 60
Fixed ammonia (% of total)	40 - 80
Oil and grease, mg/l	500 - 2,000
Sulfide and Sulfite, mg/l as S	500 - 2,000
Sulfate, mg/l as SO_4	200 - 800
Chloride, mg/l as Cl	2,000 - 6,000
Cyanide as HCN, mg/l as CN	20 - 100
Thiocyanate, mg/l as CNS	300 - 1,200
Phenols, mg/l	500 - 3,000
COD, mg/l	8,000 - 16,000
Solids - total, mg/l	Unknown
Solids - suspended, mg/l	Unknown

TABLE 4-3. FINAL COOLER WATER BLOWDOWN COMPOSITION
(SOURCE: BIBLIOGRAPHY 7)

Constitutents	Concentration Range
Ammonia-N, mg/l	200 - 400
Phenols, mg/l	500 - 1,500
BOD_5, mg/l	2,000 - 3,000
COD, mg/l	3,000 - 4,000
TOC, mg/l	800 - 1,400
Cyanide (CN), mg/l	100 - 300
Sulfide (H_2S), mg/l	10 - 40
Thiocyanate (CNS), mg/l	200 - 1,000
Solids - total, mg/l	200 - 700
Solids - suspended, mg/l	20 - 60
Oil, mg/l	10 - 40
pH	7 - 9

TABLE 4-4. LIGHT OIL PLANT (BENZOL) PROCESS WASTEWATER COMPOSITION (SOURCE: BIBLIOGRAPHY 7)

Constitutents	Concentration Range
Ammonia-N, mg/l	10 - 100
Phenols, mg/l	60 - 200
BOD_5, mg/l	300 - 600
COD, mg/l	500 - 1,000
TOC, mg/l	200 - 600
Cyanides, mg/l	10 - 60
Solids-total, mg/l	200 - 700
Solids-suspended, mg/l	30 - 70
Oil, mg/l	10 - 200
pH	5 - 8

In plants that remove hydrogen sulfide from the gas, fouling of the absorber solution is another source of contaminated wastewater. The volume of water generated from this source can range from 0.3 to 12 gallons per ton of coal (dry) depending on the removal process employed.

Concentrations representative of the effluent wastewater from a vacuum carbonate desulfurization process are:

Constituents	Concentration
Ammonia, mg/l	50
Phenol, mg/l	5
Cyanide, mg/l	1,200
Sulfide, mg/l	30
BOD_5, mg/l	1,200
COD, mg/l	1,700
TOC, mg/l	700

This effluent wastewater is usually recycled to the coke quenching station for reuse.

Coal pile runoff, another major wastewater stream from coke oven plants, has characteristics that depend on the type of coal stored. Typical wastewaters from the two types of coal generally stored in the coke oven industry are:

	High Volatile, Bituminous (38% V.M.)	Low Volatile, Bituminous (17% V.M.)
pH	6 - 7	2.5 - 7
Suspended Solids	600 - 14,000 mg/l	100 - 1,000 mg/l
	Avg. 10,000 mg/l	Avg. 500 mg/l

Other miscellaneous wastewaters originate from the following:

a. Pump and compressor seal water
b. Floor washdowns
c. Tank washings
d. Spills
e. Rain water runoff from process and storage areas
f. Wastewater from steaming or flushing of piping and equipment.

Air Emissions--

In the Byproduct coke plants, the majority of the air emissions emanate from the coke oven (including quenching) operations and consist of two types: fugitive losses, and stack emissions from the fuel burning operation (underfiring) at the coke ovens. Table 4-5 gives the quantities of air emissions from the coke ovens and quenching operations per ton of coal charged. These emission factors were developed by the EPA based on data gathered prior to 1972. Since that time, more extensive data have been acquired by the EPA. It is expected that additional pollutant factors (e.g., benzene soluble organics) may be added or others modified in the table in the near future. The calculated sulfur dioxide (SO_2) emissions in Table 4-5 are based on the assumption that the coke oven gas has not been desulfurized prior to the underfiring operation. However, many coke plants are using cleaner fuels for underfiring.

Besides the coke ovens, small amounts of fugitive emissions (containing smoke, particulates, hydrocarbons, etc.) emanate from all other unit operations/processes of the Byproduct Coke plants. Quantitative information on these losses is not available from the literature.

The types of fugitive emissions found in the unit operations/processes are as follows:

Unit Operation/Process	Contaminant
Coal Pile	Particulates
Coal Handling and Preparation	Particulates
Coke Ovens (Fugitive and Underfiring) including Quench Station	Particulates, So_2, CO, H-C, NO_x, NH_3 (see Table 4-5)
Primary Cooler	Particulates
Tar Separator, Exhauster and Tar Extractor	Odors (NH_3, organics)
Ammonia Removal	Particulates, H_2SO_4 mist and NH_3
Fine Cooler, Naphthalene Skimmer basin	Odors
Light Oil Recovery, Light Oil Refining	Particulates, odors
Gas Compressor, H_2S Removal and Sulfur Recovery.	Particulates, H_2S, SO_2

TABLE 4-5. UNCONTROLLED AIR EMISSIONS FROM COKE OVENS/QUENCHING OPERATIONS [1]

	Air Emissions, Lbs.*					
Stream	Particulates	SO_2	CO	Hydrocarbons	NO_x	Ammonia
Charging	1.5	0.02	0.60	2.5	0.03	0.02
Coking Cycle	0.1	-	0.60	1.5	0.01	0.06
Pushing/Discharging	0.6	-	0.07	0.2	-	0.10
Quenching	0.9	-	-	-	-	-
Underfiring	-	4.0 **	-	-	-	-
TOTAL:	3.1	4.02	1.27	4.2	0.04	0.18

* Based on one ton of coal input to the coke ovens.

**Coke oven gas before desulfurization is used for underfiring the ovens.

[1] "Compilation of Air Pollutant Emission Factors", 3rd Edition, EPA-AP 42.

Solid Wastes--

Solid waste sources from the Byproduct coke oven plants are:

a) Coke breeze from coke sizing and screening, quenching operations. About 70 to 100 pounds per ton of coal charged to the ovens are converted to coke breeze with the following typical composition:

	Range (wt. %)
Volatile Matter	4 - 6
Fixed Carbon	76 - 80
Ash	10 - 20
H_2O	0.5 - 5.0

Coke breeze has an economic value, and is sold or reused in many installations.

b) Coal particulates from coal pile run-off wastewater treatment. Recovered coal from the coal pile runoff could be returned to the coal pile for reuse.

c) Solid wastes from process wastewater treatment (from biological treatment system and ammonia stripping unit). Biological treatment systems yield about 7.6 pounds of dry solids per ton of coal fed.

d) Residue in the form of tar sludge generated from tar decanting in the tar separator. About 3.3 pounds of tar sludge per ton of coal fed is periodically removed as a solid waste from the tar storage tank.

Material Balance of a Typical Byproduct Coke Oven Plant

To assess the quality and quantities of products, byproducts and wastes generated from an average coke oven plant, a 5,000 TPD (coal input) plants was selected as a typical model. The material balance basis of the above plant is summarized in Table 4-6. Many of the major design assumptions including yield and analyses of different products are taken from the literature. Figure 4-1 and Table 4-7 depict the block flow diagram and overall material balance for the 5,000 TPD coke oven plant, respectively.

Tables 4-8 and 4-9 provide a summary of the air emissions and wastewater effluent from the 5,000 TPD model coke oven plant.

TABLE 4-6. DESIGN BASIS FOR A 5000 TPD BYPRODUCT COKE OVEN PLANT

1. Coal Type	Bituminous Mixture
Coal Moisture:	4.0% by wt.
Sulfur Content:	1.0% by wt.
2. Coke Ovens Operating Conditions	
Batteries:	3
Coke Ovens per battery:	85
Coal charge per oven:	20 tons
Coking cycle:	17 hours
Temperature:	900°C
Underfire excess air:	6%
3. Yields	
Products, byproducts, % wt. coal (volume, scf/ton of coal)	
Coke	70.343
Tar	5.45
Light Oil	1.102
Ammonia	0.223
Coke Oven Gas	15.661 (12,000)
Water (Liquor)	6.805
Other Gases	0.416
4. Raw Coke Oven Gas Composition	
% wt. of coal feed:	
H_2	1.366
N_2	0.385
CO_2	1.042
CO	3.154
CH_4	7.468
C_2H_4	1.529
O_2	0.717
NH_3	0.223
Tar	5.45
H_2O	6.776
C_6H_6 (equiv)	1.102
C_2N_2	0.078
CS_2	0.013
H_2S	0.325
Phenol (organics)	0.029

TABLE 4-6 (Continued)

5.	Quench Water Feed Rate:	500 gallons per ton of coke
	Evaporation Rate:	35%
6.	Weak Ammonia Liquor Recycle Rate, gal/ton of coal	1,430
7.	Wash Oil Recirculation Rate in the Light Oil Recovery Unit, gal/ton of coal	150
8.	75% of the total naphthalene in the coke oven raw gas is recovered from the final cooler skimmer basin.	
9.	Overall Sulfur Removal Through the Vacuum Carbonate System	90%

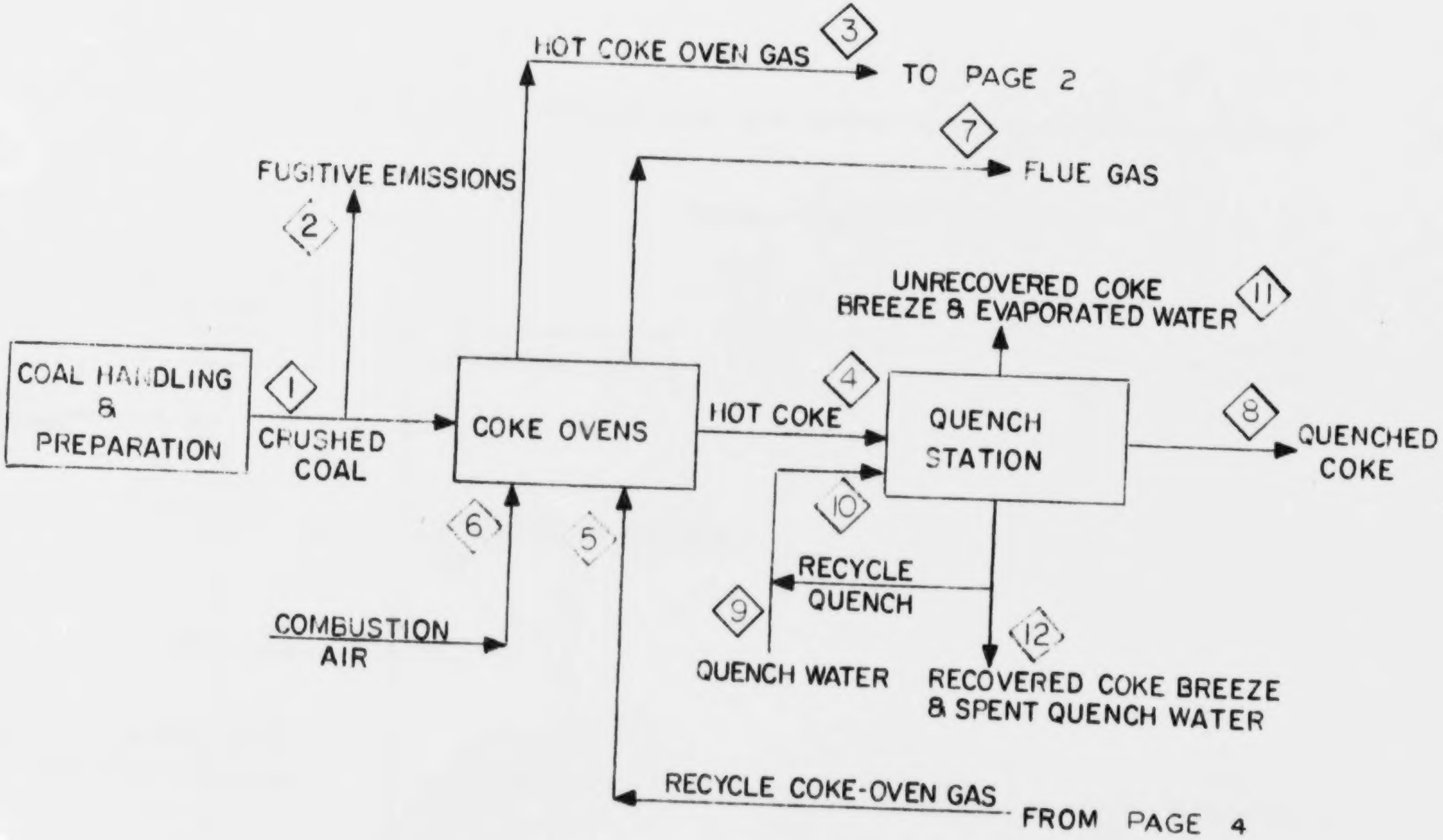
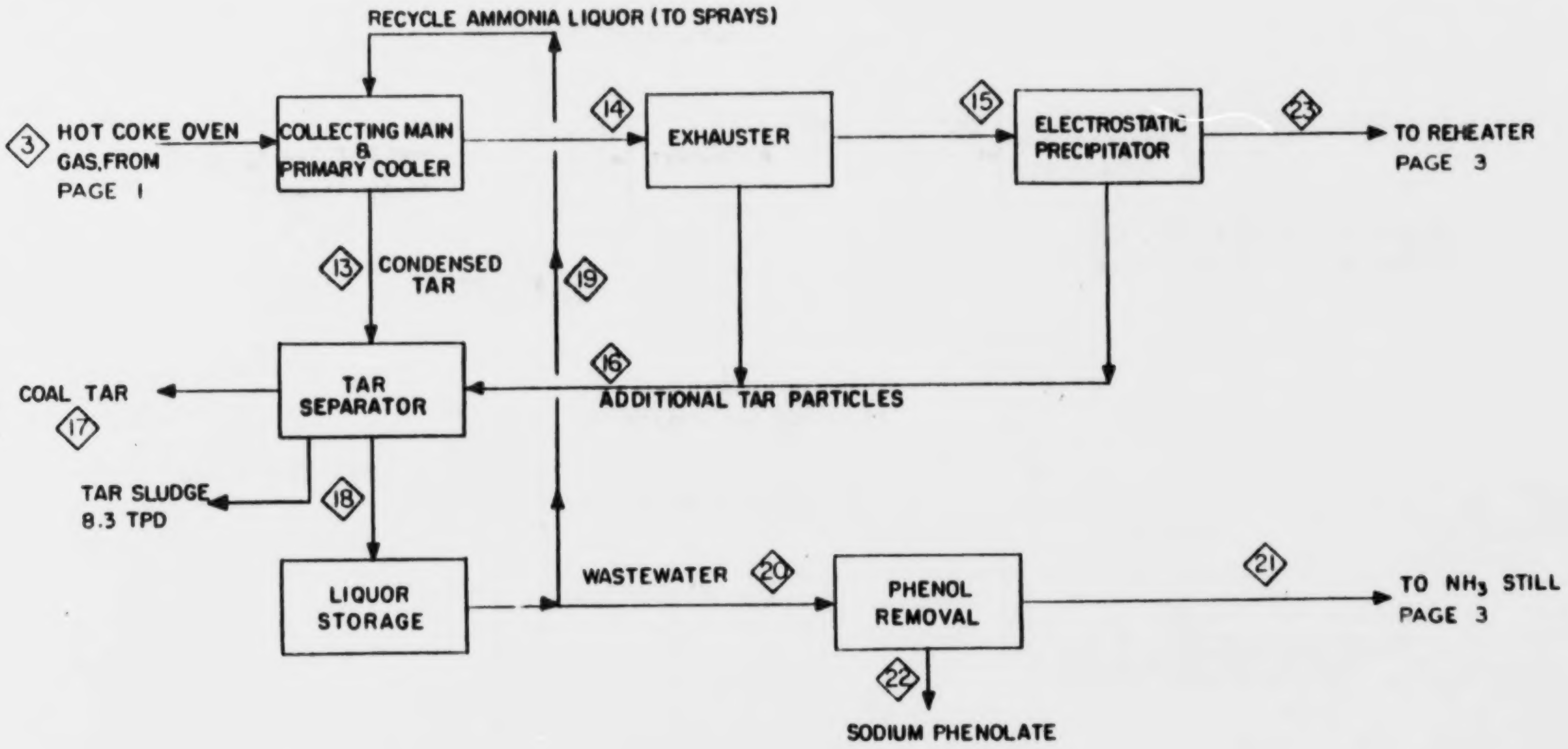

COAL HANDLING & PREPARATION
1
CRUSHED COAL
2
FUGITIVE EMISSIONS
COKE OVENS
HOT COKE OVEN GAS
3
TO PAGE 2
7
FLUE GAS
6
COMBUSTION AIR
5
RECYCLE COKE-OVEN GAS
FROM PAGE 4
HOT COKE
4
QUENCH STATION
UNRECOVERED COKE BREEZE & EVAPORATED WATER
11
8
QUENCHED COKE
10
RECYCLE QUENCH
9
QUENCH WATER
12
RECOVERED COKE BREEZE & SPENT QUENCH WATER

Figure 4-1 (Pg. 1 of 4). Detailed block flow diagram of a byproduct coke oven plant.


RECYCLE AMMONIA LIQUOR (TO SPRAYS)
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HOT COKE OVEN GAS, FROM PAGE 1
COLLECTING MAIN & PRIMARY COOLER
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EXHAUSTER
15
ELECTROSTATIC PRECIPITATOR
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TO REHEATER PAGE 3
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CONDENSED TAR
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16
COAL TAR
17
TAR SEPARATOR
ADDITIONAL TAR PARTICLES
TAR SLUDGE 8.3 TPD
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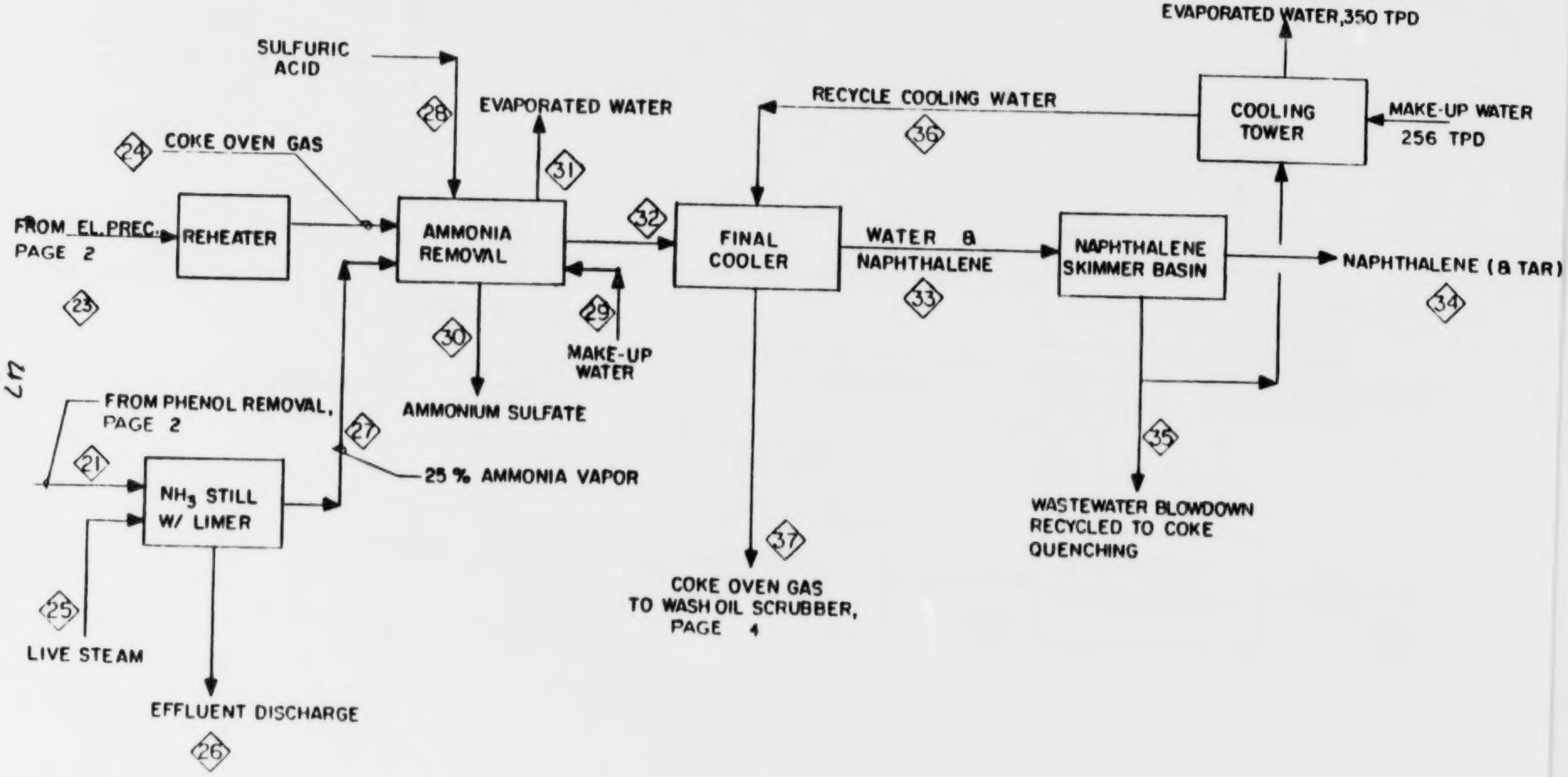
LIQUOR STORAGE
WASTEWATER
20
PHENOL REMOVAL
21
TO NH_3 STILL PAGE 3
22
SODIUM PHENOLATE

Figure 4-1 (Pg. 2 of 4). Detailed block flow diagram of a byproduct coke oven plant.



SULFURIC ACID
EVAPORATED WATER
COKE OVEN GAS
FROM EL. PREC. PAGE 2
REHEATER
AMMONIA REMOVAL
FINAL COOLER
RECYCLE COOLING WATER
COOLING TOWER
EVAPORATED WATER, 350 TPD
MAKE-UP WATER 256 TPD
WATER & NAPHTHALENE
NAPHTHALENE SKIMMER BASIN
NAPHTHALENE (& TAR)
MAKE-UP WATER
AMMONIUM SULFATE
FROM PHENOL REMOVAL, PAGE 2
NH_3 STILL W/ LIMER
25 % AMMONIA VAPOR
LIVE STEAM
EFFLUENT DISCHARGE
COKE OVEN GAS TO WASH OIL SCRUBBER, PAGE 4
WASTEWATER BLOWDOWN RECYCLED TO COKE QUENCHING
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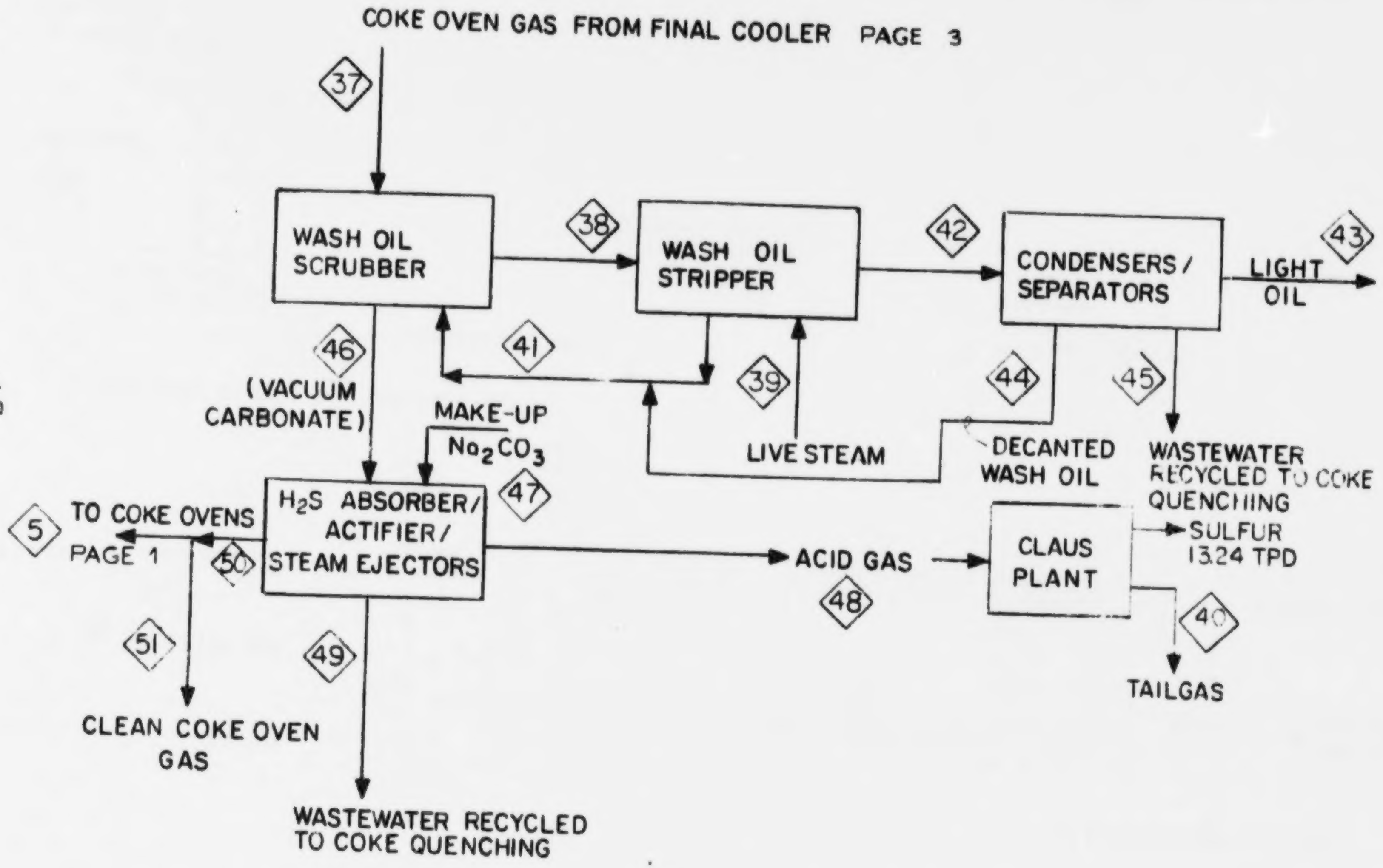
Figure 4-1 (Pg. 3 of 4). Detailed block flow diagram of a byproduct coke oven plant.


COKE OVEN GAS FROM FINAL COOLER PAGE 3
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WASH OIL SCRUBBER
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WASTEWATER RECYCLED TO COKE QUENCHING
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CLAUS PLANT
SULFUR 13.24 TPD
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TAILGAS
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CLEAN COKE OVEN GAS
WASTEWATER RECYCLED TO COKE QUENCHING

Figure 4-1 (Pg. 4 of 4). Detailed block flow diagram of a byproduct coke oven plant.

TABLE 4-7 MATERIAL BALANCE OF A 5000 TPD COKE OVEN PLANT

FLOWS, TPD

	1 Coal From Handling	2 Fugitive Emissions	3 Hot Coke Oven Gas	4 Hot Coke	5 Recycled Coke Oven Gas	6 Combustion Air	7 Flue Gas	8 Quenched Coke	9 Quench Water Makeup	10 Total Quench
Coal or Coke	4,800			3517.2				3264.9		
Tar		5.5	267.0							
Light Oil			55.1							
Ammonia		0.45	10.6							
Water	200.0		338.95		16.92		631.07	101.0	2915.0	7325.0
CO		3.18	154.5		61.8					
H_2			68.3		27.32					
N_2			19.2		7.68	3233.4	3241.04			
CO_2			52.1		19.33		614.9			
CH_4		8.7	364.6		145.84					
C_2H_4		1.8	74.7		29.88					
O_2			35.9		14.36	985.9	55.3			
C_2N_2			3.9		0.64					
CS_2			0.7		0.28					
H_2S			16.2		0.65					
Cyanides				Trace						Trace
Phenol			1.25	Trace						Trace
H_2SO_4										
$(NH_4)_2SO_4$										
Napthalene										
Wash Oil										
Na_2CO_3		0.15								
Others										
TOTAL	5,000	19.8	1463.0	3517.2	324.7	4219.3	4544	3365.9	2915.0	7325.0

(continued)

TABLE 4-7. (Continued)

	11 Unrecovered Coke Breeze and Evaporated Water	12 Recovered Coke Breeze and Spent Quench Water	13 Condensed Tar	14 C.O.G. to Exhauster	15 C.O.G. To Electro-Static Precip.	16 Additional Tar Particles	17 Coal Tar	18 Liquor to Storage	19 Recycle Liquor	20 Liquor to Phenol	21 Liquor NH Still
Coal or Coke	2.3	250.0									
Tar			244.13	22.87	2.29	22.85	258.69				
Light Oil			2.8	52.3	52.3		2.8				
Ammonia			309.65	7.95	7.95		0.06	309.59	307.0	2.59	2.59
Water	2,564.0	250.0	29,729.4	82.5	82.5		5.45	29,723.9	29,473.0	250.9	250.9
CO				154.5	154.5						
H_2				68.3	68.3						
N_2				19.2	19.2						
CO_2				52.1	52.1						
CH_4				364.6	364.6						
C_2H_4				74.7	74.7						
O_2				35.9	35.9						
C_2N_2				3.5	3.5						
CS_2				0.7	0.7						
H_2S				16.2	16.2						
Cyanides		Trace	40.49					40.49	40.15	0.34	0.34
Phenol		Trace	89.32	0.50	0.50	0.75		89.32	88.57	0.75	
H_2SO_4											
$(NH_4)_2SO_4$											
Napthalene											
Wash Oil											
Na_2CO_3											
Others											
TOTAL	2,566.3	500.0	30,415.8	955.8	935.2	23.60	267.0	30,163.3	29,908.7	254.6	253.8

(continued)

TABLE 4-7. (Continued)

	22	23	24	25	26	27	28	29	30	31
	Sodium Phenolate	C.O.G. to Reheater	C.O.G. to NH_3 Removal	Steam to NH_3 Still	Wastewater From NH_3 Still	25% NH_3 to NH_3 Removal	H_2SO_4 to NH_3 Removal	Makeup H_2O to NH_3 Removal	Ammonium Sulfate	Evaporation H_2O from NH_3 Removal
Coal or Coke										
Tar		0.02	0.02							
Light Oil		52.3	52.3							
Ammonia		7.95	7.95		0.03	2.57				
Water		82.5	82.5	42.25	285.45	7.70	10.00	254.8	0.04	9.95
CO		154.5	154.5							
H_2		68.3	68.3							
N_2		19.2	19.2							
CO_2		52.1	52.1							
CH_4		364.6	364.6							
C_2H_4		74.7	74.7							
O_2		35.9	35.9							
C_2N_2		3.5	3.5							
CS_2		0.7	0.7							
H_2S		16.2	16.2							
Cyanides					0.34 **					
Phenol	0.75*	0.50	0.50							
H_2SO_4							29.99			
$(NH_4)_2SO_4$									40.39	
Napthalene										
Wash Oil										
Na_2CO_3										
Others										
TOTAL	0.75	933.0	933.0	42.25	285.82	10.27	39.99	254.8	40.4	9.95

*Phenol content of sodium phenolate

(continued)

** About 50 mg/l free cyanide and the remainder as thiocyanates.

TABLE 4-7. (Continued)

	32 C.O.G. to Final Cooler	33 Water & Naphthalene Final Cool	34 Naphthalene & Tar	35 Wastewater Blowdown	36 Recycle Cooling Water to Final Cooler	37 C.O.G. to Wash Oil Scrubber	38 Light Oil to Stripping	39 Live Steam to Light Oil Stripper	40 Tailgas	41 Recycled Wash Oil
Coal or Coke										
Tar	0.02	0.02	0.02							
Light Oil	52.3					51.32	53.96			5.2
Ammonia	0.11	4.04		0.11	3.93					
Water	345.0	11,130.		209.	10827.0	42.30	250	250		
CO	154.5					154.5				
H_2	68.3					68.3				
N_2	19.2					19.2				
CO_2	52.1					52.1				
CH_4	364.6					364.6				
C_2H_4	74.7					74.7				
O_2	35.9					35.9				
C_2N_2	3.5					3.5				
CS_2	0.7					0.7				
H_2S	16.2					16.2				
Cyanides		3.31		0.09	3.22		0.02			
Phenol	0.50	16.55		0.45	16.1	0.05	0.05			
H_2SO_4										
$(NH_4)_2SO_4$										
Napthalene		0.98	0,98							
Wash Oil							2602.44			2602.44
Na_2CO_3										
Others										
TOTAL	1187.63	1154.9	1.0	209.65	10850.25	883.27	2906.47	250	31.1	2607.64

(continued)

TABLE 4-7. (Continued)

	42 Light Oil to Condenser/ Separators	43 Light Oil from Condenser/ Separators	44 Wash Oil from Condenser/ Separators	45 Wastewater from Condenser/ Separators	46 C.O.G. to H_2S	47 Na_2CO_3	48 Acid Gas	49 Waste-Water from H_2S	50 Clean C.O.G.	51 Product
Coal or Coke										
Tar										
Light Oil	48.76	48.76								
Ammonia					2.57			2.57		
Water	250.00			250	42.30	7.3		232.3	42.3	25.38
CO					154.5				154.5	92.7
H_2					68.3				68.3	40.98
N_2					19.2				19.2	11.52
CO_2					52.1		3.78		52.1	32.76
CH_4					364.6				364.6	218.76
C_2H_4					74.7				74.7	44.82
O_2					35.9				35.9	21.54
C_2N_2					3.4				1.58	0.95
CS_2					0.7				0.7	0.42
H_2S					16.2		14.58		1.62	0.97
Cyanides	0.02			0.02			1.54	0.28		
Phenol	0.05			0.05	Trace			Trace		
H_2SO_4										
$(NH_4)_2SO_4$										
Napthalene										
Wash Oil	2.44		2.44							
Na_2CO_3						0.27		0.27		
Others										
TOTAL	301.27	48.76	2.44	250.07	834.47	7.57	19.9	235.42	815.5	490.8

TABLE 4-8 SUMMARY OF AIR EMISSIONS - 5000 TPD BYPRODUCT COKE OVEN PLANT

(Emissions are in tons per day.)

Stream	Total Flow (TPD)	Particulate Matter	SO_2	CO	H-C	NO_x	NH_3	CO_2	N_2	H_2O	H_2S
Fugitive Emissions	19.8	5.5 (Tar)	0.05	3.18	10.52	0.10	0.45				
Flue Gas	4544		1.69		55.3			614.9	3241.04	631.07	
Unrecovered Coke Breeze and Evaporated Water	2566.3**	2.3 (Coke Breeze)								2564.0	
Evaporated Water (Cooling Tower & Others)	360.0									360.0	
Claus Tail Gas	31.103		0.096					5.32	25.508		.179*
Totals	7,521.203	7.8	1.836	3.18	65.82	0.10	0.45	620.22	3,266.548	3,555.07	.179

* Includes .015 and 0.096 TPD of CS_2 and COS, respectively.

** Fugitive emissions from cooling tower and coke quenching with contaminated water may lead to substantial air pollution problem. The quantity of these pollutants has not been ascertained.

TABLE 4-9. SUMMARY OF PROCESS WASTEWATER - 5000 TPD BYPRODUCT COKE OVEN PLANT

(Wastewater Contaminants, tons/day)

Stream No.	Total Flow (TPD)	Water	Phenol	Cyanides	Ammonia
20	254.58	250.9	0.75	0.34	2.59
35	209.65	209.0	0.45	0.09	0.11
45	250.07	250.0	0.05	0.02	-
49	232.58	232.3	Trace	0.28	-
Totals	946.88	942.20	1.25	0.73	2.7

Solid wastes quantities generated by the model plant are the following (water free basis): 250 tons/day coke breeze; 8.3 tons/day of tar sludges; and 19 tons/day of bio-sludges.

Process Description--

Bituminous coal containing about 30 percent volatile matter and 4 percent water is crushed to about 1/8-inch size in a hammer mill and then fed to the coke ovens. Three batteries of coke ovens, each battery containing 85 ovens, are provided. Coking temperature and cycle are 900°C and 17 hours, respectively. At the end of the coking cycle, hot coke is quenched with water in a quench station.

From the coal handling, preparation and coke oven operations, approximately 19.8 TPD of fugitive emissions are lost to the atmosphere. In the quenching operation, 2.3 TPD of fine coke breeze is emitted to the atmosphere as well as large amounts of evaporated quench water.

During coking of the coal, raw coke oven gas is evolved containing a mixture of gases, entrained solids, various products and pollutants such as cyanide, hydrogen sulfide and phenol.

The crude gas leaves the ovens through standpipes and passes into a gas collecting main. There, the temperature of the gas is reduced from approximately 800 to 1,300°F to about 175 to 200°F by spraying with recycled ammonia liquor. This reduction in gas temperature causes condensation of approximately 75 percent of the tar in the gas together with a small portion of ammonia. The condensed ammonia appears as excess ammonia liquor, which is sent to an ammonia stripping operation.

From the collecting main, the gas passes to the primary coolers where it is cooled to about 85 to 104°F by ammonia liquor spray. This cooling removes additional tar, and again, a small portion of the total ammonia in the gas. The gas is next conducted to an exhauster (positive displacement type) which serves not only to compress the gas but also to remove tar by the high-speed swirling motion imparted to the gas.

The gas passing through the exhausters still contains traces of tar fog which is further reduced by electrostatic precipitators. The tar drains from the bottom of the precipitators into a settling pit which also collects the tar removed from the collecting main and primary coolers. It is then pumped from the pit and transferred to a storage tank where excess water is decanted. This tar, containing about 2 percent moisture, is sold to chemical companies for processing and recovery of valuable aromatic compounds.

The excess ammonia liquor which results from gas cooling in the collecting main and primary coolers is pumped from liquor storage to a phenol removal unit. Here, phenol is extracted from the liquor through use of a solvent such as a light oil fraction, and recovered as sodium phenolate by treatment with caustic.

The liquor is then sent to an ammonia stripping unit, where ammonia is removed by contact with live steam. The stripped liquor is discharged to waste treatment (physical/chemical or biological), and the vapor stream, containing 25 weight percent of ammonia, joins the detarred coke oven gas stream in entering the ammonia removal unit.

In the ammonia removal unit, the combined gas stream flows through an absorbent tower into which is sprayed a dilute sulfuric acid solution. The sulfuric acid reacts with the ammonia to produce ammonium sulfate. The ammonium sulfate eventually reaches a saturation point in the solution, and begins to crystallize. The crystal slurry is pumped to a centrifuge, where a cake is produced and dried in a rotary drum dryer to about a 0.1 weight percent moisture content.

In some plants, a crystallizer is equipped with a barometric condenser which uses a large quantity of water. An example of this process is the Wilputte process.

After the ammonia removal unit, the gas passes through the final coolers where direct contact water is used to cool the gas to a temperature of 70 to 90°F. A major portion of the naphthalene condenses out of the gas due to this cooling. The naphthalene is recovered from the cooling water at the settling basin where it is skimmed off as it rises to the top. It is either added to the tar or is processed further to produce a commercial product.

The cooled coke oven gas is scrubbed with a petroleum wash oil. The gas comes in direct contact with the wash oil in one or more scrubbing towers containing packing and interlocking sprays. The flow of gas and wash oil is counter-current in each tower, and counter-current over the entire multi-tower system. The wash oil absorbs the light oil so that the benzolized wash oil contains 2 to 3 percent light oil. From 90 to 95 percent of the light oil content of the gas is recovered in this operation

The wash oil is debenzolized by steam distillation. The carryover of wash oil into the light oil is kept to about 5 percent and the debenzolized wash oil contains 0.2 percent light oil. The mixture of light oil and steam exists the top of the stripping column, is condensed, and separated. The light oil is sent to the Houdry LITOL process for refining of benzene and other components.

The gas, after being stripped of light oil, is next sent to the desulfurization unit for sulfur removal. Many desulfurization processes are available, however, the Vacuum Carbonate process has moved into commercial prominence.

In the Vacuum Carbonate process, the gas is contacted counter-currently with a solution of sodium carbonate in an absorber tower to remove the hydrogen sulfide and other impurities such as hydrogen cyanide. The foul solution from the base of the absorber is circulated over the actifier where the hydrogen sulfide is removed by counter-current stripping with water vapor under vacuum. The actified solution is pumped from the base of the actifier through a cooler to the absorber to complete the cycle. The acid gas, Stream No. 48, is sent to a Claus plant for sulfur recovery.

After desulfurization, approximately 40 percent of the product gas is returned to the coke ovens as a fuel source.

OTHER COKE OVEN PROCESSES

Beehive Process

The only product recovered from the Beehive ovens is the coke itself. Approximately 1,200 pounds of coke per ton of coal are recovered.

Raw waste loads from the Beehive oven are a function of coking time, water use systems, moisture and volatility of the coal, and carbonizing temperature of the ovens. However, the raw waste is affected most by the type of water use systems, that is, once-through or recycle. Table 4-10 summarizes the net plant raw waste load from three selected plants. Raw waste loads are presented only for the critical parameters which include ammonia, BOD_5, cyanide, phenol and suspended solids.

For the Beehive coke plant, the majority of the emissions emanate from the oven door during watering-out and drawing of the coke. The estimated nature and quantity of these emissions based on one ton of coal input are:

TABLE 4-10. CHARACTERISTICS OF BEEHIVE COKE PLANT WASTES
(Net Plant Raw Waste Load) [1]

Characteristics	Plants		
	1	2	3
Flow, l/kkg	2,040	2,040	513
Ammonia, mg/l	0.33	0	0
BOD, mg/l	3.00	0	0
Cyanides, mg/l	0.002	0	0
Phenol, mg/l	0.011	0	0
Suspended Solids, mg/l	-	29	722

---

[1] Data obtained from Bibliography 21.

Particulates	-	200 lbs
Carbon Monoxide	-	1 lb
Hydrocarbons	-	8 lbs
Ammonia	-	2 lbs

Low Temperature Processes

In low temperature coke manufacturing applications, the main objective is to obtain maximum yields of liquid products and semi-cokes containing from 8 to 20 percent volatile matter. Here again, the characteristics and yields of the various products and byproducts depend upon the coal, the temperature and the treatment.

One ton of coal would yield on an average the following products and byproducts:

	Pounds
Semi-coke (char)	1,440
Tar (15.8 gal)	150
Ammonia, anhydrous	5
Light oil (2.5 gal)	16
Gas (3,720 scf)	250
	1,861

The balance (139 lbs) probably consists mostly of condensed moisture, small amounts of pollutants (e.g. particulates, phenols) in the process wastewater and the fugitive air emissions. However, this assumption needs verification, since the data varies among different references in the literature.

The typical clean gas composition is as follows:

Constituent	Volume %
Co_2	9.0
C_nH_m	8.0
CO	5.5
H_2	10.0
CH_4 and Homologs	65.0
N_2	2.5

No information on the wastewater and air emission was available from the literature reviewed. There is no commercial or developmental low temperature coke oven process in the United States.

SECTION 5

COAL GASIFICATION PROCESSES AND THEIR WASTE CHARACTERISTICS

COAL GASIFICATION PROCESSES

In contrast to coke oven gas which is produced from distillation (carbonization) of coal, coal gasification process gases are produced by a combination of the following mechanisms:

- Distillation of coal by heating;
- Reaction of solid coal with oxygen and steam; and
- Reaction of various intermediate gases.

Four principal chemical reactions occur in a gasification reactor:

		Standard Enthalpy Change @ 1,200°K
(1)	$C + H_2O \rightleftharpoons CO + H_2$	- 32,457 cal/g.mol
(2)	$CO + H_2O \rightleftharpoons CO_2 + H_2$	+ 7,838 " " "
(3)	$C + 2H_2 \rightleftharpoons CH_4$	+ 21,854 " " "
(4)	$C + 1/2\ O_2 \rightleftharpoons CO$	+ 26,637 " " "

Reaction (3) demonstrates the formation of methane, which is favored at low temperatures (below 1,000°F) and high pressures. High temperature and low pressure gasification processes (e.g., K-T process) do not produce much methane in the gasifier reactor.

Besides the above four reactions, other chemical reactions and devolatilization of coal in the gasifier result in the formation of byproducts and trace pollutants, such as:

- Gases containing reduced sulfur compounts - (H_2S, COS, CS_2, etc.)
- Gases containing nitrogen compounds - (NH_3, HCN, etc.)
- Hydrocarbons
- Heavy metals/trace contaminants.

Most of the above mentioned byproducts and pollutants are also found in the coke oven raw gases.

Approximately 68 different gasification processes have been used commercially in the past or are currently under development. Most of these systems, however, were retired or did not achieve commercial status because of the availability of less costly natural gas. Prominent gasification processes (fourteen) of current and potential interest are shown in Table 5-1 along with their expected products and byproducts.

Principal sub-divisions of coal gasification processes are differentiated by low-, intermediate- and high-temperature operations. The type of reactor bed (fixed, fluidized or entrained) is also another operating variable. The low-temperature and fixed-bed processes tend to show a complete product and byproduct slate similar to the coke oven process. As the temperature of gasification increases, recoverable quantities of heavier tars begin to diminish in preference to increasing lighter molecular weight products. Operating pressure also affects the yields, as shown in Table 5-1. As the pressure increases, the product slate tends towards the heavier molecular weight substances.

A coal gasification plant consists of many unit operations/processes. A block flow diagram of a hypothetical synthetic natural gas plant is shown in Figure 5-1. The plant is comprised of the following major areas:

1. Coal Storage, Preparation and Feeding;
2. Gasification and Gas Cleaning;
3. Product Upgrading (Methanation);
4 Byproduct Recovery and Upgrading; and
5. Waste Treatment.

The basic steps to produce a synthetic natural gas (SNG) fuel are as follows: First, coal is prepared to the desired size by crushing, removing fines and drying the coal (if necessary). The coal is then either fed to the gasifier or, if it is a caking coal and the process cannot operate with such a coal, it is pretreated with heat to prevent the formation of coke.

The coal is then reacted with oxygen and steam in the gasifier. (Note: If the final product gas is to be a low-Btu gas, then air can be used instead of oxygen.) Pertinent chemical reactions and the devolatilization step mechanism which generates the raw gases within the gasifier have been previously discussed.

TABLE 5-1

COAL GASIFICATION PROCESSES PRODUCT/BY–PRODUCT AND FUEL SYSTEM SIMILARITIES

LEGEND:

P – Product/By-Product present in recoverable quantities.

Neg. – Negligible or small amounts present.

– Stream present in traces.

N.A. – Information not available, not complete, or not reported at this time.

	CLASSIFICATION OF FUEL SYSTEMS													
	Low Temperature Fixed Bed				Intermediate Temperature Fluidized Bed				High Temperature Entrained Bed		Dolomite Acceptor		Coal Pyrolysis	
	Low Pressure	Intermediate Pressure			Low Pressure	Inter–mediate Pressure	High Pressure		Low Pressure	High Pressure	Intermediate Temperature Intermediate Pressure		Entrained Inter. Temp. Low Pressure	Fluid Bed Inter. Temp. Inter. Pressure
Products/By–Products	Wellman – Galusha	Lurgi	BGC/Lurgi Slagging Gasifier	Pressurized Stirred Fixed Bed – Morgantown	Winkler	U – Gas	Synthane	Hygas	Koppers–Totzek	Bi–Gas	CO_2 Acceptor	Westinghouse–Advanced Gasifier	Battelle – Ash Agglomerating	Garretts Coal Gasification
High BTU Gas – SNG	P	P	P	–	P	–	P	P	P	P	P	–	P	P
Low (Intermediate) BTU Gas	P	P	P	P	P	P	–	–	P	–	–	P	P	P
H_2S – Acid Gas/Sulfur	P	P	P	P	P	P	P	P	P	P	P	P	P	P
Ammonia	P	P	P	P	N A	P	P	P	Neg.	P	P	N.A.	P	N.A.
Phenols	P	P	P	P	Neg.	Neg.	P	P	–	–	N.A.	–	–	–
Naphthas/Benzenes	N.A.	P	P	–	–	N.A.	P	P	–	–	N.A.	–	–	–
Tar Oils/Light Oils	P	P	P	P	–	Neg.	P	P	–	–	N.A.	–	–	–
Tars	–	P	P	P	–	Neg.	P	–	–	–	N.A.	–	–	P
Char/Unreacted Coal	P	–	–	P	P	P	P	P	–	–	P	–	–	P
Ash/Slag	–	P	P	P	–	–	–	–	P	P	–	P	P	–

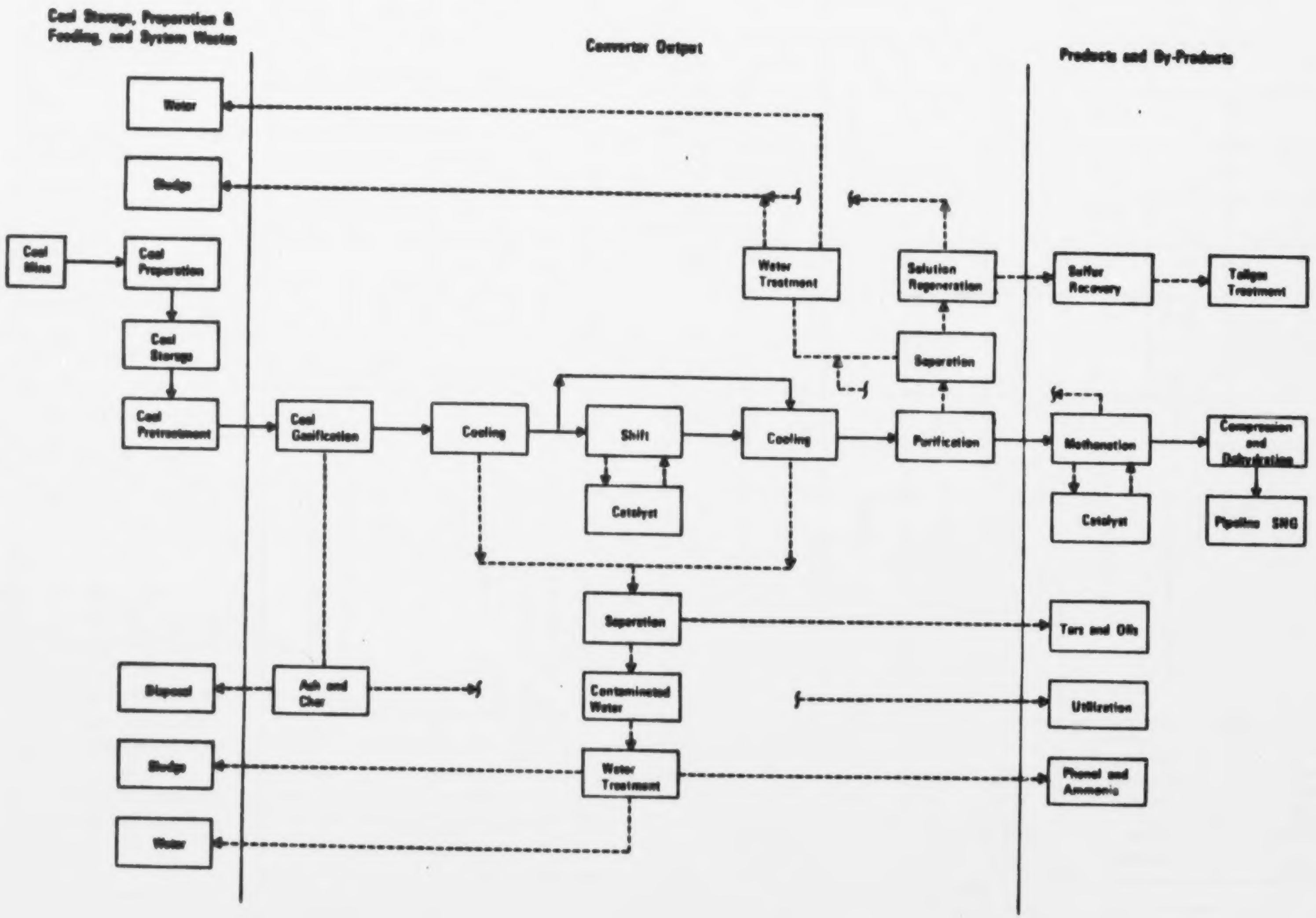

Coal Storage, Preparation & Feeding, and System Wastes
Converter Output
Products and By-Products
Water
Sludge
Coal Mine
Coal Preparation
Coal Storage
Coal Pretreatment
Coal Gasification
Cooling
Shift
Catalyst
Cooling
Water Treatment
Solution Regeneration
Separation
Purification
Sulfur Recovery
Tailgas Treatment
Methanation
Catalyst
Compression and Dehydration
Pipeline SNG
Separation
Tars and Oils
Contaminated Water
Utilization
Water Treatment
Phenol and Ammonia
Disposal
Ash and Char
Sludge
Water

Figure 5-1. Hypothetical coal gasification flow diagram.

The raw gases are next processed through the gas cleaning and purification steps to remove tar, particulate matters and sulfur compounds.

The raw gases produced in the gasifier do not have the proper proportion of CO and H_2 necessary to form SNG or synthesis gas. A shift catalyst reactor unit is introduced to produce appropriate gas mixtures. In the shift reactor, any desired ratio of carbon monoxide and hydrogen can be achieved by varying the amounts of steam and carbon dioxide as demonstrated by the following reaction:

$$CO + H_2O \rightleftarrows H_2 + CO_2,\ \Delta H^{o}_{25^{o}C} = 9.9\ \text{Kcal/mol}$$

(Note: If hydrogen is the desired final product, the carbon monoxide is all converted to carbon dioxide and hydrogen; carbon dioxide is then scrubbed from the gas by any of several available processes.)

If a high Btu gas (SNG) is the objective, then the required ratio of hydrogen to carbon monoxide is 1:3. The following chemical reaction (called methanation) is employed:

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O,\ \Delta H^{o}_{25^{o}C} = 49.3\ \text{Kcal/mol}$$

The methanation reaction is highly exothermic; consequently, heat removal methods are the dominating feature of the different developing processes.

The Byproduct recovery and waste treatment aspects of the coal gasification processes will vary for each specific process, since the recoverable quantities of byproducts and the waste characteristics are dependent on gasifier operating conditions. The feed coal characteristics also significantly affect the quantities of products and byproducts generated from a process. Adequate literature information is unavailable to establish the effects of coal types on the distribution of products and byproducts for different gasification processes. Table 5-2 shows the quantities of products and byproducts generated by a few selected processes.

Figure 5-2 illustrates the Byproduct recovery scheme and the distribution of the various byproducts from a Lurgi plant that will produce 288 SCFD of synthetic pipeline quality gas. A sizable portion of the byproducts are absorbed in, or condensed with, the organic and aqueous condensates as the gases are quenched with water and then cooled. The heavier tars separate out first in the gasifier waste heat boiler and are called "tarry gas liquor." Further downstream, in the gas cooling section, the tar oils with the remaining

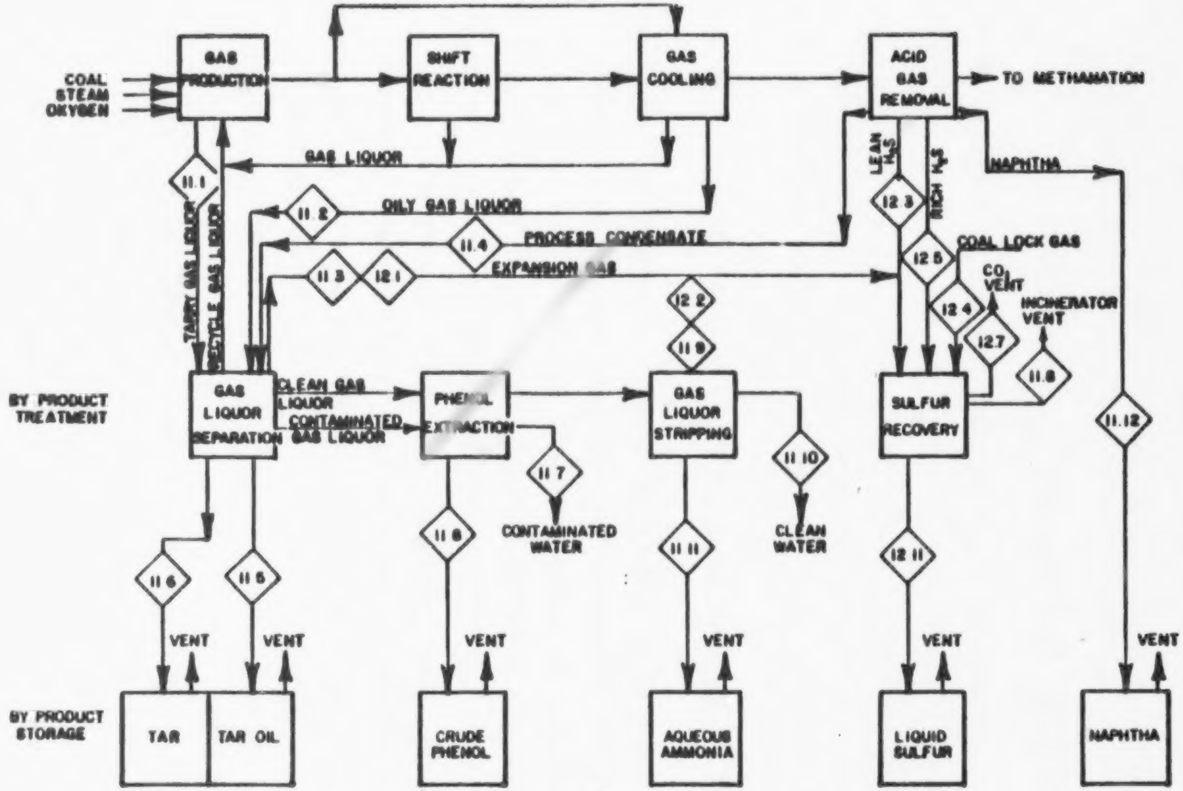

GAS PRODUCTION
COAL
STEAM
OXYGEN
SHIFT REACTION
GAS COOLING
ACID GAS REMOVAL
TO METHANATION
GAS LIQUOR
OILY GAS LIQUOR
PROCESS CONDENSATE
EXPANSION GAS
TARRY GAS LIQUOR
RECYCLE GAS LIQUOR
LEAN H2S
RICH H2S
NAPHTHA
COAL LOCK GAS
CO2 VENT
INCINERATOR VENT
11.1
11.2
11.3
11.4
12.1
12.2
11.9
12.3
12.5
12.4
12.7
11.8
11.12
BY PRODUCT TREATMENT
GAS LIQUOR SEPARATION
CLEAN GAS LIQUOR
CONTAMINATED GAS LIQUOR
PHENOL EXTRACTION
GAS LIQUOR STRIPPING
SULFUR RECOVERY
11.7
CONTAMINATED WATER
11.10
CLEAN WATER
11.6
11.5
11.8
11.11
12.11
VENT
BY PRODUCT STORAGE
TAR
TAR OIL
CRUDE PHENOL
AQUEOUS AMMONIA
LIQUID SULFUR
NAPHTHA

Figure 5-2. Byproduct from Lurgi Plant.

TABLE 5-2. PRODUCTS/BYPRODUCTS OF DIFFERENT COAL GASIFICATION PROCESSES

(SOURCE - Bibliography 35)

Product/Byproducts	Wellman Galusha	Lurgi	Koppers Totzek	Bumines Stirred Bed	Winkler	Synthane	Hygas
Product Gas, SCFD x 10^6	28.4	288	524	995	912	250	260
Heating Value (Btu/SCF)	170	(SNG)	290	160	280	(SNG)	(SNG)
Sulfur, lb/hr	177	15,600	23,600	24,200	50,400	11,400	55,500
Tars, lb/hr	1,153	88,800	Neg.	75,600		43,200	
Tar Oil, lb/hr		48,600	Neg.				
Phenol, lb/hr	120	11,300	Neg.		Neg.	4,000	1,300
Ammonia, lb/hr (anhydrous)	219	21,400	Neg.	11,100	To Claus	13,200	11,300
Hydrocarbon, lb/hr		20,000 (naphtha)				7,400 (BTX, naphtha)	39,800
Char/Ash, lb/hr (Slag)	1,768	476,000 (ash)	24,400 (ash, slag)	114,100 (ash)	372,500 (char)	362,000 (char)	139,000 (char)
Coal, lb/hr x 10^6	0.021	1.94	0.7	0.7	1.68	1.18	1.06
Feed Coal	Bitum.			W. Ky. #9	Lignite	Pitts Seam	Ill.#6
Sulfur Content (%)	3.9	1.07	3.8	3.9		1.6	4.75

Note: "SNG" signifies Synthetic Natural Gas.

tars condense out, forming the "oily gas liquor." In the acid gas removal step, H_2S and naphtha separate. Naphtha goes directly to a storage tank. H_2S-containing acid gases are further processed to recover the sulfur. Table 5-3 gives the material balance for the gas liquor treatment.

Acid Gas Removal and Sulfur Recovery

The acid gas removal unit removes sulfur compounds, carbon dioxide and any other material which would interfere with the methanation or synthesis step that follows. The unit processes involve chemical or physical absorption of the acidic materials in a suitable liquid with subsequent desorption of the acid gases at a lower pressure (in some cases higher temperature) to regenerate the absorbent.

Among the many acid gas removal processes, the following are the most widely considered for coal conversion systems:

Chemical Processes	Physical Processes
Hot Carbonate System	Rectisol (Methanol Solvent)
Amine System	Selexol (Dimethoxy Tetraethylene Glycol)
Stretford Process	

In the coke oven industry, only the chemical solvent type acid gas removal processes have been commercially utilized. The physical solvent type processes will be more applicable when the raw gas is at a higher pressure (which obviously cannot be related to the coke oven process since it operates near atmospheric pressure). Detailed discussions of the coke oven gas desulfurization processes and their applicability to coal conversion systems are given in Section 7.0. Table 5-4 shows the acid gas removal processes that have been considered in a recent study(39) for various gasification processes.

The Stretford process not only removes acid gases from the gas; but, it also recovers byproduct sulfur. Therefore, it is also considered a sulfur recovery process. Other processes listed above, produce a concentrated acid gas stream (rich in hydrogen sulfide concentration) which requires further control through a sulfur recovery and tail gas unit to meet air pollution control regulations. The two most common sulfur recovery processes are the Claus and Stretford. The Stretford process is economic when the acid gas

TABLE 5-3. MATERIAL BALANCE FOR GAS LIQUOR TREATMENT

STREAM NUMBER	11.1	11.2	11.3	11.4	11.5	11.6	11.7	11.8	11.9	11.10	11.11	11.12
Stream Description	Tarry Gas Liquor	Oily Gas Liquor	Expansion Gas	Process Condensate	Tar Oil	Tar	Contaminated Gas Liquor	Crude Phenol	Acid Gas	Clean Water	Aqueous Ammonia	Naphtha
Phase	Liquid	Liquid	Gas	Liquid	Liquid	Liquid	Liquid	Liquid	Gas	Liquid	Liquid	Liquid
Component (lb/hr)												
Water	165,000	1,180,000	2,030	103,000	--	--	164,000	--	8,870	1,190,000	82,000	--
Tar	79,900	8,900	--	--	--	88,800	--	--	--	--	--	--
Tar Oil	14,600	34,000	--	--	48,600	--	--	--	--	--	--	--
Recoverable Crude Phenol	210	11,100	--	--	--	--	--	--	--	--	--	--
Unrecoverable Phenol & Organic	130	4,100	--	--	--	--	--	--	--	--	--	--
Ammonia	--	21,600	--	--	--	--	--	--	--	240	21,400	--
H_2S	300	300	315	--	--	--	--	--	280	--	10	--
CO_2	17,200	54,800	59,700	--	--	--	--	--	8,570	--	3,660	--
CO	70	--	70	--	--	--	--	--	--	--	--	--
CH_4	40	--	50	--	--	--	--	--	--	--	--	--
Monohydric Phenols	--	--	--	--	--	--	3	9,100	--	24	--	--
Polyhydric Phenols	--	--	--	--	--	--	70	1,600	--	900	--	--
Other Organics	--	--	--	--	--	--	60	560	--	3,200	--	--
Contained Sulfur	--	--	--	--	(73)	(240)	--	--	--	--	--	--
Naphtha	--	--	--	--	--	--	--	--	--	--	--	20,000
TOTAL (lb/hr)	277,450	1,314,800	62,165	103,000	48,600	88,800	164,133	11,260	17,720	1,194,364	107,070	20,000

TABLE 5-4. ACID GAS REMOVAL PROCESSES FOR COAL GASIFICATION SYSTEMS
(SOURCE - BIBLIOGRAPHY 39)

Gasification Process	% H_2S in acid gas feed (on dry basis)	Preferred Acid Gas Process	Type of S Guard
Lurgi	1.10	Rectisol	Zinc or Iron Oxide
Synthane	1.50	Hot Carbonate (Benfield)	Zinc or Iron Oxide
Bigas	14.6	Hot Carbonate (Benfield)	Zinc or Iron Oxide
Hygas	29.8	Rectisol	Zinc or Iron Oxide
Koppers-Totzek	23.1	Methyl diethanolamine	Not needed
U-Gas	17.9	Selexol	Not needed
Winkler	15.0	Hot Carbonate (Benfield)	Not needed

contains less than 15 percent H_2S, whereas the Claus process is more economical above a 15 percent H_2S inlet concentration. Both Claus and Stretford have been utilized in coke oven plants and should have applications in coal conversion systems.

The sulfur content of the gas leaving the acid gas absorption system is decreased further, usually by reaction with iron oxide or zinc oxide. This step is necessary to protect the methanation or synthesis catalyst, which is highly sensitive to sulfur compounds. In the coke oven plants, the iron oxide process is frequently used to remove sulfur compounds.

Waste Characteristics and Comparisons

At present, the nature of the waste characteristics from coal gasification and liquefaction plants have been described mostly in qualitative terms. Much of the published quantitative information is based on pilot systems which may not be indicative of future commercial systems. The characteristics of waste streams that are predicted for commercial systems, therefore, are based on engineering analysis of the coal conversion processes and related operations, such as coke ovens and coal preparation plants.

Wastewaters--

The following major wastewaters are associated with coal gasification systems:

1. Quench and condensate waters from gasification;
2. Wastewater from the shift and methanation (or synthesis) units;
3. Coal pile runoff; and
4. Miscellaneous waters, e.g., storm water runoff, boiler blowdown, etc.

Detailed characteristics of these wastewaters for the different types of coal gasification processes are not available. However, many studies are in progress under DOE and EPA sponsorship to develop additional information. Coal pile and storm water runoffs will contain relatively less pollutants than the process wastewaters.

The compositions of the quench and condensate waste streams from the gasification process are expected to be dependent on the coal conversion process, the operating conditions, and the coal type. The limited experimental data available indicate that those gasification processes which produce byproducts similar to coke ovens (e.g. tars, tar oils, naphtha) will generate wastewaters similar to the Byproduct coke oven process. This was illustrated by the wastewater composition shown in Table 1-3 (abstracted from Tables 4-2, 5-3 and 5-5).

High temperature and low pressure gasification processes that do not generate much byproduct (e.g. K-T process), on the other hand, will generate low concentrations of contaminants in the process wastewater and are not comparable to the Byproduct coke oven process.

Coal type and composition have significant effects on the process wastewater. This is illustrated in Table 5-5, where the effect of various coals on Synthane wastewaters are shown. These data were obtained from a laboratory scale operation of the Synthane process.

Approximately 60 to 80 percent of the toal organic carbon in the coke oven and coal conversion wastewater appears to be phenolic in nature consisting of monohydric, dihydric and polyphenols. Singer, et al. have recently reported the breakdown of the phenolics and other organics in the coal conversion wastewater(58).

Gaseous Waste Streams--

The following major gaseous streams are associated with coal gasification processes:

1. Raw product gas from the gasifier;
2. Acid gases from the acid gas removal unit;
3. Cooling tower emissions;
4. Flue gases from the utility boilers; and
5. Fugitive emissions, e.g. from coal pile, compressors, storage tanks, etc.

The characteristics of the raw product gas and the acid gases have been discussed previously. Characteristics of the flue gases from the utility boilers will be dependent on the type of fuel used in the boilers, e.g., raw coal, processed clean product gas, or raw product gas.

No data is available on the fugitive emissions. Fugitive emissions sources are: cooling towers; compressors; valves; flanges; coal pile; wastewater and solid handling units; etc. The fugitive emissions are expected to

TABLE 5-5. PROCESS WASTEWATER ANALYSIS FROM SYNTHANE GASIFICATION OF VARIOUS COALS

(All values in mg/l, except pH; Bibliography 26)

	Illinois No. 6 Coal	Wyoming Sub-bit. Coal	North Dakota Lignite	Western Kentucky Coal	Pittsburgh Seam Coal
pH	8.6	8.7	9.2	8.9	9.3
Suspended Solids	600	140	64	55	23
Phenol	2,600	6,000	6,600	3,700	1,700
COD	15,000	43,000	38,000	19,000	19,000
Thiocyanate	152	23	22	200	188
Cyanide	0.6	0.23	0.1	0.5	0.6
NH_3	8,100	9,520	7,200	10,000	11,000
Chloride	500	-	-	-	-
Carbonate	6,000	-	-	-	-
Bicarbonate	11,000	-	-	-	-
Total Sulfur	1,400	-	-	-	-

- Data not available

contain hazardous species that are in the raw product gas such as hydrogen sulfide, carbon monoxide, and hydrogen cyanide. These pollutants are also present in the coke oven fugitive emissions.

Solid Wastes-

The following are major solid waste sources from a coal gasification plant:

1. Ash or slag from the gasifier;
2. Particulates from coal preparation;
3. Ash from coal burning in the Utility Boiler;
4. Wastewater treatment sludges; and
5. Spent catalyst from the methanation (or synthesis) reactor and shift converter.

The ash or slag from the gasifier accounts for the largest quantitative source of solid wastes, and these wastes contain the most numerous types of contaminants including many heavy metals. Solid wastes of similar composition are not generated in the coke oven industry.

Characteristics of the particulate matter from coal preparation and the sludges from wastewater treatment will have some similarity between the two industries.

SECTION 6

COAL LIQUEFACTION PROCESSES AND THEIR WASTE CHARACTERISTICS

COAL LIQUEFACTION PROCESSES

The objectives of the U.S. coal liquefaction development programs are to develop viable processes that will produce low-sulfur and low-ash products from coal to be used as boiler fuels, heating oils, gasoline and chemical feedstocks. Although none of the processes currently under development has achieved commercial status, several have reached the pilot plant stage. Table 6-1 shows the processes of current and potential interest along with their expected products and byproducts.

Since coal has only about 5 percent hydrogen compared to 9 to 11 percent for fuel oils and 14 percent for gasoline, converting solid coal to liquid fuels requires increasing the hydrogen content relative to carbon (H/C) in the coal. Coal liquefaction processes increase the H/C ratio either by adding hydrogen to the coal or by removing part of the carbon as is done in the coal pyrolysis processes. Pyrolysis processes that developed from coke oven technology, however, yield small quantities of liquid products, since large amounts of gaseous and solid char products are also produced. Table 6-1 shows the four types of coal liquefaction processes: catalytic hydrogenation, solvent extraction, hydrocarbonization, and pyrolysis.

In the catalytic hydrogenation and solvent extraction processes, the coal is dissolved in process-derived solvent, and molecular hydrogen is added via a hydrogen donor solvent. Three of the processes under these categories (SRC-I, H-Coal and Exxon Donor Solvent processes) have, thus far, received the most concerted development effort. They will be discussed subsequently in detail.

Pyrolysis processes are similar to coal coking in that the coal is heated to remove tars, gas and other volatiles leaving a coal char that is largely carbon. Coal pyrolysis processes usually operate at low pressures (20 to 50 psia) and moderately high temperature (approximately 1,600°F).

TABLE 6-1

COAL LIQUEFACTION PROCESSES–PRODUCT/BY–PRODUCT AND FUEL SYSTEM SIMILARITIES

LEGEND:

P – Product/By-Product present in recoverable quantities.

Neg.– Negligible or small amounts present.

– Stream present in traces.

N.A. – Information not available, not complete, or not reported at this time.

	CLASSIFICATION OF FUEL SYSTEMS								
				Solvent Extraction		Hydrocarbonization		Pyrolysis	
	Catalytic Hydrogenation			Non-Catalytic Solvent Hydrogenation	Catalytic Solvent Hydrogenation	Intermediate Temperature	High Temperature	Low Temperature Fluid Bed	Intermediate Temperature Entrained Bed
Products/By--Products	H–Coal	Synthoil	Gulf Catalytic Coal Liquefaction	Solvent Refined Coal (SRC)	EXXON Donor Solvent Process	Coalcon Hydrocarbon-ization	Clean Coke Multi-Product Process	Char, Oil Energy Development (COED)	Garrett Process
High B.T.U. Gas – SNG, LPG, ethylene, hydrocarbon, product gas.	P	P	N.A.	P	P	P	P	–	P
Low (Intermediate) BTU Gas – Fuel Gas, Synthesis Gas	–	–	N.A.	–	–	–	–	P	P
H_2S Acid Gas/Sulfur	P	P	P	P	P	P	P	P	P
Ammonia	P	P	P	P	N.A.	P	P	N.A.	N.A.
Phenols	Neg.	N.A.	P	P	N.A.	P	P	P	–
Benzenes	N.A.	N.A.	P	–	N.A.	P	P	P	–
Naphtha, Gasoline	P	–	P	P	P	P	P	–	–
Syncrudes	P	P	P	–	–	–	–	P	P
Middle Distillates, Fuel Oil	P	–	P	P	P	P	–	–	P
Gas Oils, Neutral Oils, Chemical Oils	P	–	P	–	P	P	P	–	–
Residual Fuel Oils	P	P	P	P	–	–	–	–	–
Tars (Tar Acids and Tar Bases)	–	–	–	–	–	P	P	–	P
Solvent Refined Coal	–	–	–	P	–	–	–	–	–
Char/Coke/Unreacted Coal	P	P	N.A.	P	–	P	P	P	P
Ash/Slag	P	–	N.A.	P	P	–	P	–	–

Hydrocarbonization is a refinement of the coal pyrolysis process. It consists of carbonization of coal and thermal cracking of the heavy coal liquids (tars) in a hydrogen atmosphere to produce fuel oil, distillate and fuel gas. Hydrocarbonization operates at both a moderate pressure (500 psi) and temperature (1000°F). The pyrolysis and hydrocarbonization processes are the direct development of the Byproduct coke oven process. Their product/byproduct slates are very similar. The waste characteristics are expected to be similar also. However, insufficient data exist to verify this hypothesis.

Figure 6-1 shows the block flow diagram of a hypothetical coal liquefaction process (hydrogenation or extraction type). The principal features of the process are:

1. Hydrogenation reaction unit;
2. Separation unit (where gaseous products are separated from the liquid and solid products);
3. Filtration (or solid separation) unit;
4. Acid gas treatment and sulfur recovery unit; and
5. Product fractionation and upgrading units.

The feed coal is crushed, dried, and slurried with a coal-derived solvent (produced by the process) and fed to the liquefaction reactor in admixture with gaseous hydrogen. Gas, liquid and solid phases are produced in the reactor by a series of complex chemical reactions which include decomposition (depolymerization), hydrogenation, and rearrangement of the organic coal structure.

The reactor effluent containing liquid products, solids and gases are next separated for product and byproduct recovery. The separation schemes vary for each process.

Separation of ash and unreacted coal from viscous coal liquids is a difficult problem common to all liquefaction processes and has been the focus of considerable development effort. Many techniques are being investigated, including filtration, centrifugation, fractionation, and solvent separation.

In coal liquefaction processes, distinct patterns of product slates (Table 6-1) do not readily emerge as in the coal-gasification processes.

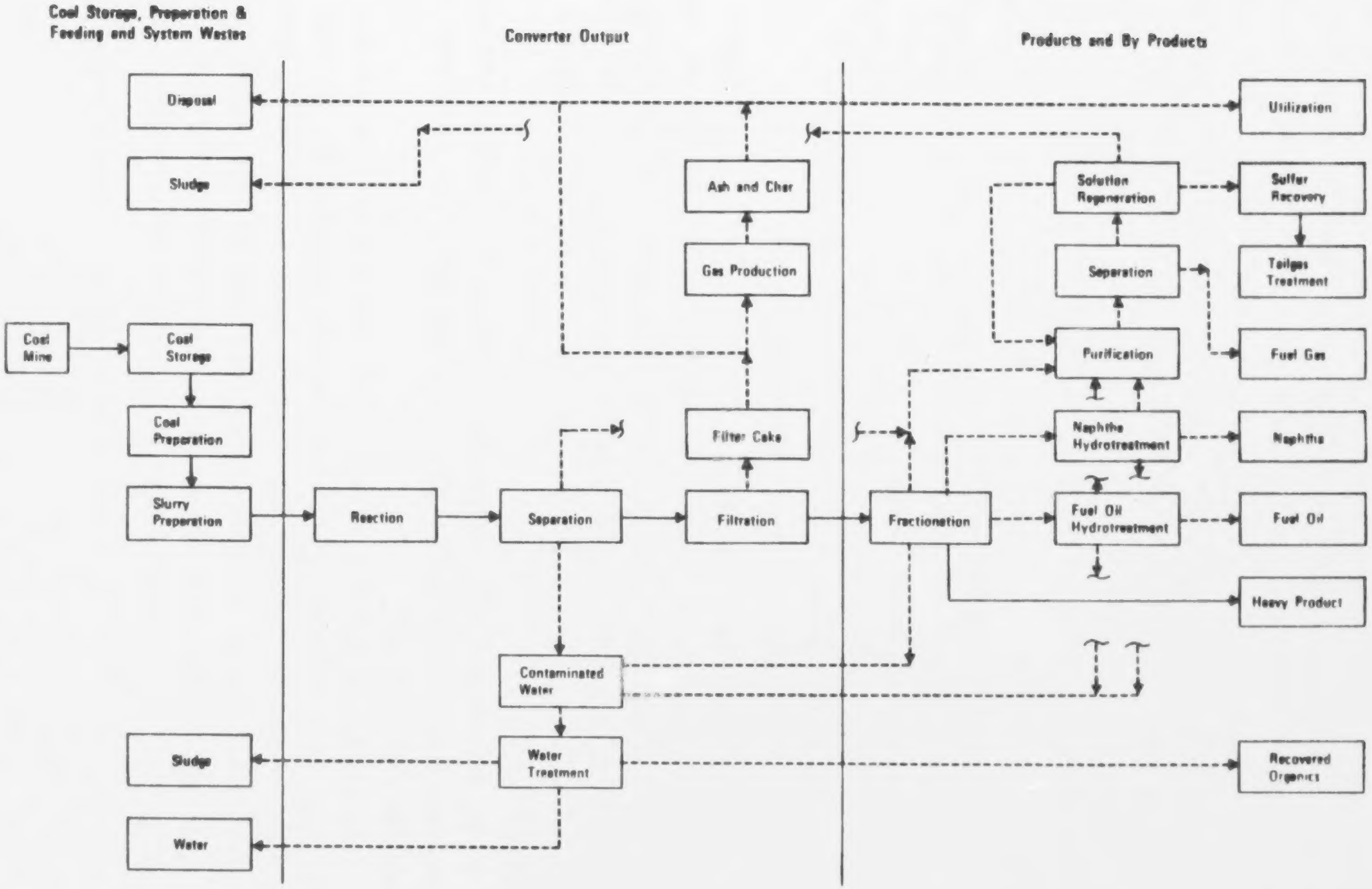

Coal Storage, Preparation & Feeding and System Wastes
Converter Output
Products and By Products
Disposal
Sludge
Coal Mine
Coal Storage
Coal Preparation
Slurry Preparation
Sludge
Water
Reaction
Separation
Contaminated Water
Water Treatment
Ash and Char
Gas Production
Filter Cake
Filtration
Fractionation
Solution Regeneration
Separation
Purification
Naphtha Hydrotreatment
Fuel Oil Hydrotreatment
Utilization
Sulfur Recovery
Tailgas Treatment
Fuel Gas
Naphtha
Fuel Oil
Heavy Product
Recovered Organics

Figure 6-1. Hypothetical coal liquefaction flow diagram.

However, the following observations can be made:

- All liquefaction processes produce an acid gas stream which will contain sulfur and other contaminants. In this regard, they are similar to coal gasification processes which also produce an acid gas stream. Consequently, H_2S removal and sulfur recovery will be required for all coal processing plants.
- Liquid product distribution shows a range from syncrudes to naphtha and gas oils. However, all will contain varying amounts of sulfur, nitrogen, and metal contaminants which will have to be removed by subsequent upgrading treatments. Only the solvent refined coal (SRC-I) process yields a solid fuel. In all other processes, additional hydrogenation results in the formation of liquid products.
- Almost all the processes produce a char (coke and unreacted coal combined with ash) byproduct with some fuel value. These byproducts will require additional processing (e.g., specially designed combustion units) to utilize the carbon value. This will increase the energy efficiency of the conversion process.
- Phenols and/or ammonia will be present in the aqueous waste streams in most cases and could be recovered as byproducts.

It is difficult to give quantitative yield data and waste characteristics of coal liquefaction process since these are dependent on many variables such as:

1. Coal type and composition;
2. Hydrogen consumption;
3. Liquefaction process and its operating conditions;
4. Hydrogen generation method;
5. Product specifications; and
6. Power generation method.

Unlike the coke oven process which uses a specific type of coal mix, various coals can be used to produce liquid products. Yields will vary depending on the coal composition. For example, the liquid yield is about 2.6 barrels per ton (B/T) of dry Illinois #6 coal, and about 2.3 B/T from Wyoming coal for the Exxon Donor Solvent Process(25).

Hydrogen consumption in the process has a direct bearing on the quantity and quality of the liquefied products. As an example, the hydrogen consumption for the SRC-I process is about 2 weight percent of moisture-free coal; whereas, it is approximately 4 weight percent for the H-Coal and the EDS process. Less hydrogen consumption in the SRC-I process is the reason for its production of mostly solid refined coal and a lesser amount of liquid products. If additional hydrogen is consumed in the SRC system (by additional hydrogenation in the reactor), more liquid products will be generated, as in the SRC-II process.

The liquefaction process and its operating conditions have a significant effect on product type as illustrated in Table 6-2 for the three major processes. Other variables such as reactor detention time, catalyst utilization, solvent type and reactor type have an impact on product/byproduct yield. The liquefaction reactor design for the SRC-I and Exxon Donor Solvent (EDS) process is an upward plug flow type; whereas, the H-Coal uses an ebullated bed where a catalyst is also added. The EDS process uses a solvent oil which has been catalytically hydrogenated in a fixed bed reactor.

The method of hydrogen generation affects the product/byproduct slate and the environmental aspects of the plant. Since the cost of hydrogen is a key economic factor in coal liquefaction processes, various schemes are under consideration to generate hydrogen from the byproducts of the coal liquefaction (e.g., gasification of char and solid wastes, steam reforming of fuel gas). The hydrogen generation plant is a large unit in the overall coal liquefaction complex and its contribution to the plant waste streams would be significant.

The power generation plant is another large contributor to the general waste streams. Methods of power generation will vary from plant to plant. In order to decrease the complexity and number of variables, the power generation unit and other auxiliary units such as the oxygen plant, the water treatment unit etc. have not been considered in this report.

As the foregoing discussion shows, the potential variables are so numerous that the material balance and quantitative yield data for a specific liquefaction process can be presented meaningfully only when all the different variables are considered in detail. (Also, comparison of one process with another will not be meaningful if these variables are not fixed.) This has been done for an example coal liquefaction plant for the SRC-I process.

TABLE 6-2. OPERATING CONDITIONS OF THREE LEADING COAL LIQUEFACTION PROCESSES

Process	Reactor Pressure (psia)	Reactor Temp. (°F)	Hydrogen Consumption (scf/bbl product)	Product Type
H-Coal	2,700-3,000	850	4,000-7,000	Syncrude or fuel oil, fuel gas
Exxon Donor Solvent Process	1,500-2,500	700-900	5,000-6,000	Fuel oil, naphtha, fuel gas
SRC-I	1,000-2,400	625-850	1.5-3.0 wt% of MF Coal	Solid boiler fuel, naphtha, fuel gas

SRC-I PROCESS MATERIAL BALANCES

Design Basis

Based on the published information on the process conditions and operating results from the Wilsonville and Fort Lewis SRC pilot plants, a conceptual design for a 20,000 TPD coal feed SRC-I plant was prepared and is discussed here. The data obtained at Wilsonville in Runs 70 through 81 and at Fort Lewis in Runs 4 through 9, using Kentucky #9 and #14 coals and solvent of boiling range 450 to 780°F, were used to develop the design basis. Table 6-3 summarizes the design basis.

Overall Material Balance

An overall flow diagram and material balance for the SRC-I process are shown in Figure 6-2 and Table 6-4 respectively. The basic SRC-I process consists of seven modules:

Coal receiving and preparation;
Slurry preparation, preheating and dissolving;
Hydrogen recovery;
Precoating and filtration;
Solvent recovery;
Product recovery and solidification; and
Hydrogen manufacture

Coal is dried, crushed, mixed with coal-derived solvent and hydrogen, preheated, and introduced into a dissolver (liquefaction) reactor where coal is reduced to liquid products. The resultant process stream is flashed to remove hydrocarbon gases. Unreacted coal and ash solids are next removed from the liquid slurry by precoat filtration. The filter cake is sent to the hydrogen generation module where the Koppers-Totzek gasification process will be used to generate hydrogen. The filtrate, containing SRC liquid and the solvent, is next sent to the product recovery module where fractionation and solidification are used to obtain the SRC solid product.

TABLE 6-3. DESIGN BASIS FOR A 20,000 TPD COAL FEED SRC-I PLANT

1. Coal Type:	Kentucky 9-14 Colonial Mine	
Unground Coal Moisture:	9.2 wt %	
2. Ground Coal Analysis		
A. Proximate Analysis (Dry Basis)	Wt.%	
Volatile Matter	39.8	
Fixed Carbon	49.8	
Ash	10.4	
High Heating Value (MF)		12,929 Btu/lb
Moisture (wt %)	2.0	
B. Ultimate Analysis (Dry Basis)		
Carbon	70.4	
Hydrogen	5.1	
Nitrogen	1.4	
Chlorine	0.1	
Sulfur	3.4	
Ash	10.4	
Oxygen	9.2	
C. Sulfur Forms		
Pyritic	1.5	
Sulfate	0.2	
Organic	1.7	
3. Operating Conditions		
Coal Conc. % MF	38.4	
Space rate lbs/hr-ft^3, MF	75.0	
Dissolver Outlet Pressure, psig	1650.0	
Hydrogen Purity, Mol %	87.0	
Hydrogen Partial Pressure, psig		
Preheater Inlet	1450.0	
Dissolver Outlet	870.0	
4. Yields		
Conversion, % MAF coal	91.2	
Hydrogen Consumption, % MF Coal	1.95	
Yields, % MF Coal:		
CO	(-0.14)	
CO_2	0.64	
H_2S	1.81	
C_1	1.40	
C_2	0.76	
C_3	0.76	
C_4	0.16	
C_5	0.17	
IBP-350°F	2.92	
350°F - 450°F	7.58	
450°F - EP	2.11	
SRC	61.66	
Unconverted Carbon	7.86	
Ash	10.15	
H_2O	4.11	
Sulfur in SRC, %	0.96	

TABALE 6-3 (Cont'd)

5. Organic Sulfur Removal: 57.5 wt%

6. N_2 and O_2 Removal:

	In Feed Coal Wt %	In SRC Wt %	% Removal
N_2	1.36	1.72	22
O_2	9.32	4.44	71

7. Recycle Solvent Boiling Range: 450 - 780°F

8. Filter Cake Composition (Feed to H_2 Plant)

	Wt %
C	46.38
H	3.36
N	0.90
Cl	0.02
S	6.17
O	4.40
Ash	38.77

9. Physical Properties:

A. Sp. Gr. of Various Coal Slurries

Conc. %	25	25	38	38
Temp., °F	60	150	60	150
Sp. Gr.	1.083	1.065	1.133	1.106

B. Sp. Gr. of Process Solvent (450-780°F)

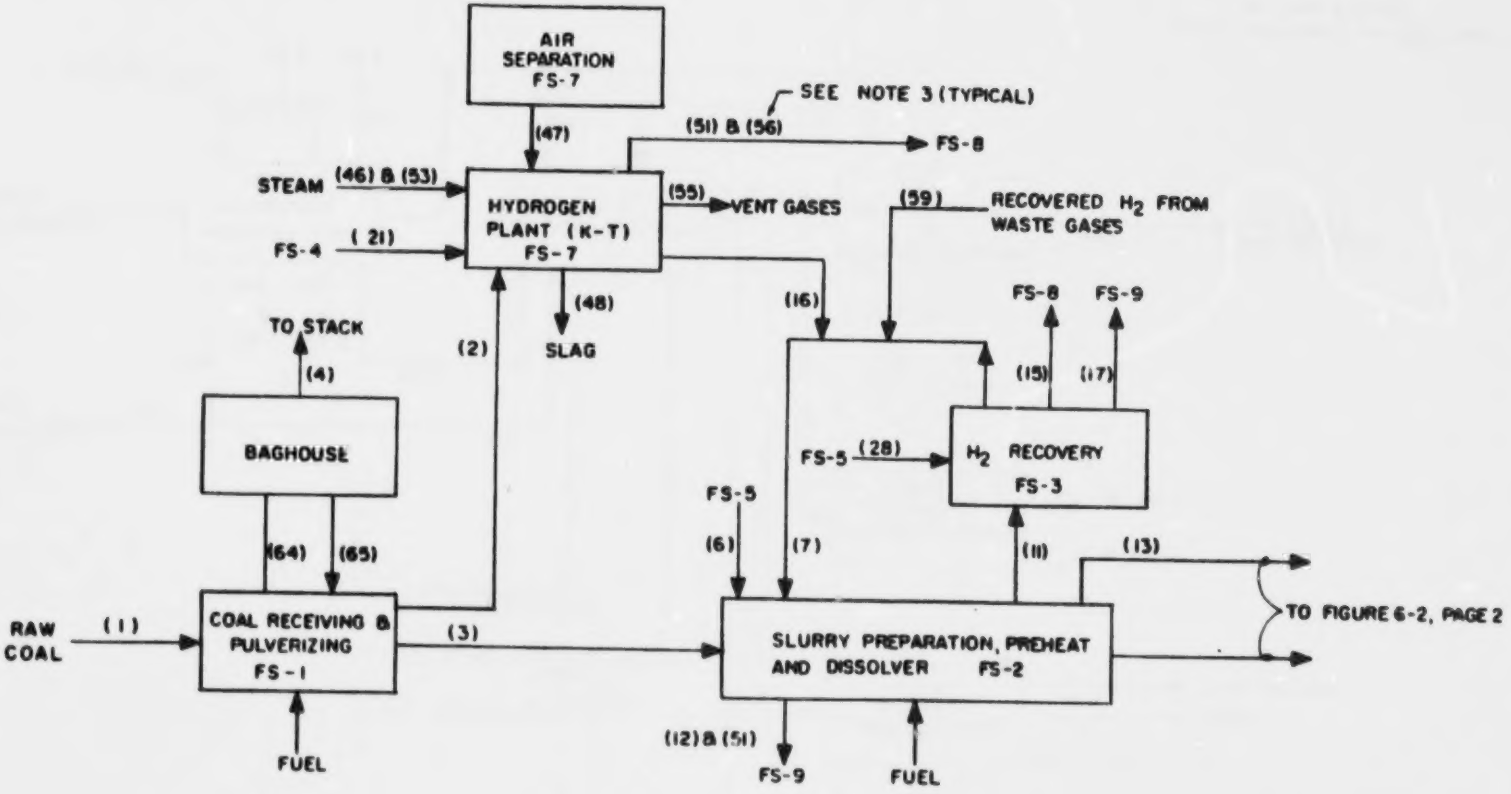
Temp., °F	60	150	200	250
Sp. Gr.	1.025	0.980	0.972	0.955

C. Viscosity of Coal Slurries

Conc. %	25	25	25	38.5	38.5	38.5
Temp. °F	85	125	165	85	125	165
Visc., CP	55	35	21	177	70	62

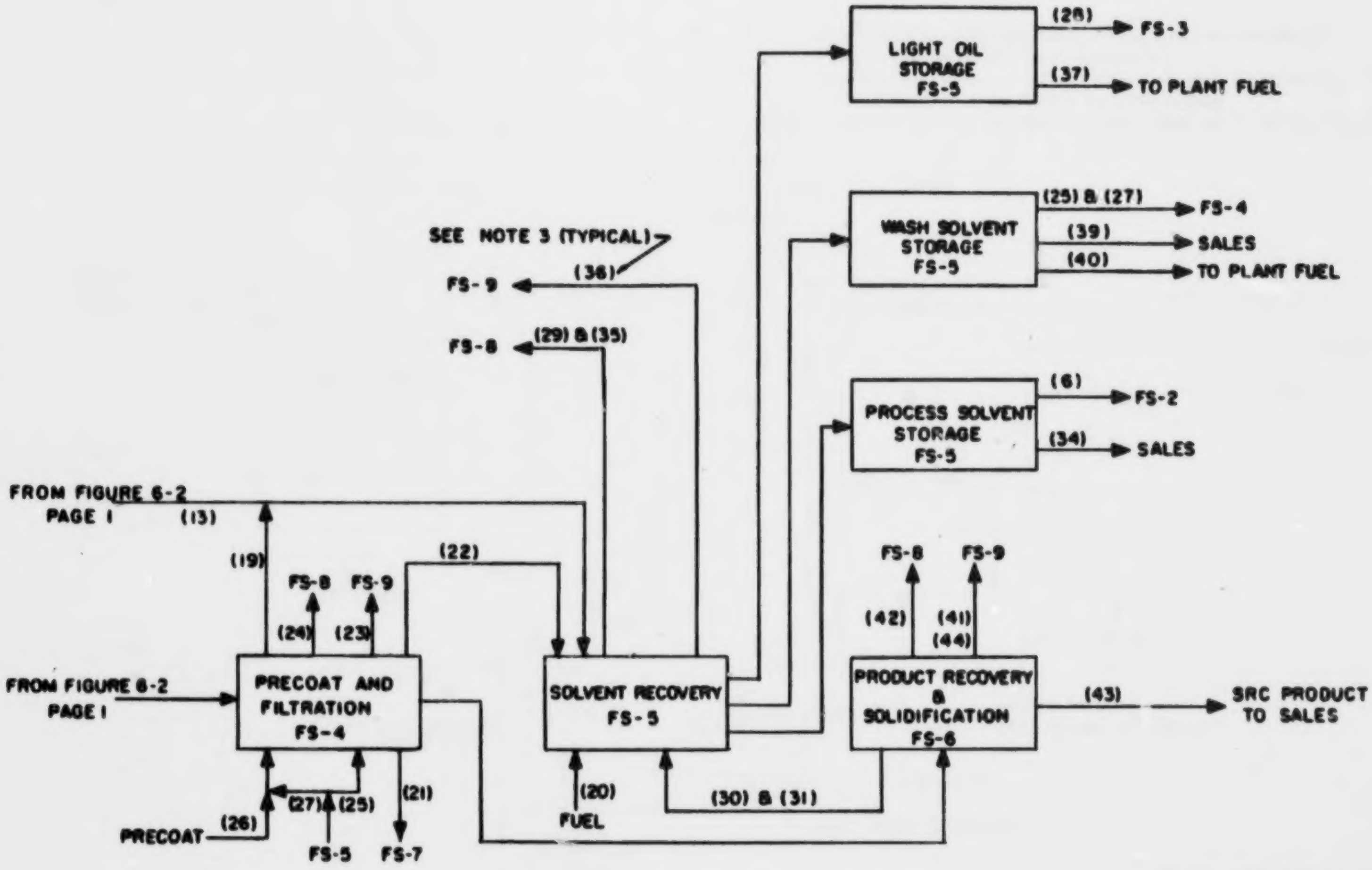
D. Properties of Liquid Products

Product	Liquid, BP°F	API°	BP°F	MW	BTU/lb
Light Oil	IBP-350	15.9	320	115	19,000
Wash Solvent	350-450	10.0	400	130	18,000
Process Solvent	450-780	4.6	567	170	17,000
SRC		-22.6	1300	750	15,800


AIR
SEPARATION
FS-7
(47)
SEE NOTE 3 (TYPICAL)
(51) & (56)
FS-8
STEAM
(46) & (53)
HYDROGEN
PLANT (K-T)
FS-7
(55)
VENT GASES
FS-4
(21)
(59)
RECOVERED H_2 FROM
WASTE GASES
(48)
SLAG
(16)
FS-8
FS-9
TO STACK
(4)
(2)
(15)
(17)
BAGHOUSE
FS-5
(28)
H_2 RECOVERY
FS-3
FS-5
(6)
(7)
(11)
(13)
(64)
(65)
RAW
COAL
(1)
COAL RECEIVING &
PULVERIZING
FS-1
(3)
SLURRY PREPARATION, PREHEAT
AND DISSOLVER FS-2
TO FIGURE 6-2, PAGE 2
FUEL
(12) & (51)
FS-9
FUEL

NOTE: 1. FS-8 (ACID GAS TREATMENT UNIT) AND FS-9 (WASTEWATER TREATMENT UNIT) ARE NOT INCLUDED IN THIS FIGURE.
2. STREAMS GOING TO FS-8 AND FS-9 ARE GASEOUS EMISSIONS AND AQUEOUS WASTES, RESPECTIVELY.
3. NUMBERS IN PARENTHESES ARE STREAM NUMBERS.

Figure 6-2 (Pg. 1 of 2). Overall flow diagram: 20,000 TPD coal feed SRC-I process.


LIGHT OIL STORAGE FS-5
(28)
FS-3
(37)
TO PLANT FUEL
WASH SOLVENT STORAGE FS-5
(25) & (27)
FS-4
(39)
SALES
(40)
TO PLANT FUEL
SEE NOTE 3 (TYPICAL)
(38)
FS-9
(29) & (35)
FS-8
PROCESS SOLVENT STORAGE FS-5
(6)
FS-2
(34)
SALES
FROM FIGURE 6-2 PAGE 1
(13)
(19)
(22)
FS-8
FS-9
(24)
(23)
FROM FIGURE 6-2 PAGE 1
PRECOAT AND FILTRATION FS-4
SOLVENT RECOVERY FS-5
FS-8
FS-9
(42)
(41)
(44)
PRODUCT RECOVERY & SOLIDIFICATION FS-6
(43)
SRC PRODUCT TO SALES
(27)
(25)
(21)
(26)
PRECOAT
FS-5
FS-7
(20)
FUEL
(30) & (31)

NOTE: FOR NOTE 1-3 SEE PAGE 1
OF THIS FIGURE

Figure 6-2 (Pg. 2 of 2). Overall flow diagram: 20,000 TPD coal feed SRC-I process.

TABLE 6-4. OVERALL MATERIAL BALANCE: 20,000 TPD SRC-I PLANT
(All flow rates are in tons per hour)

Stream No.	1	2	3	4	5 & 12	6	7	10	11	13
Hydrogen							45.812	2.03	27.61	0.27
CO							2.99	0.37	1.46	0.03
CO_2							7.93	1.60	10.61	0.96
H_2S							4.29	1.61	12.28	5.17
O_2										
N_2							7.08	3.31	3.77	
C_1							30.63	2.92	37.41	1.75
C_2							3.42	0.82	7.75	1.07
C_3							1.23	0.59	5.53	1.33
C_4							0.05	0.19	0.46	0.71
C_5							0.01	0.24	0.21	0.96
Light Oil							0.62	8.36	0.02	16.14
Wash Solvent								25.06		36.96
Process Solvent						1306.67		795.93		528.00
SRC								504.26		
Coal	776.83	45.99	730.83	0.012				64.27		
Ash/Slag	92.52	5.48	87.04	0.001				83.00		
Precoat										
H_2O/Steam	88.08	1.05	16.67	70.36	44.61			5.48	0.17	
Ammonia										
H_2S										
Total	957.43	52.52	834.54	70.37	44.61	1306.67	104.06	1500.04	107.28	593.35

TABLE 6-4 (Cont'd)

Stream No.	14	15	16	17	19	20	21	22	23	24
Hydrogen	26.44	1.17	16.09		1.98	0.05				
CO	1.34	0.12	1.64		0.35	0.02				
CO_2	7.47	3.14	0.46		1.53	0.07				
H_2S	4.29	7.99			1.52	0.09				
O_2										0.0
N_2	3.54	0.23	3.39		3.26	0.05				0.0
C_1	26.62	10.79			2.83	0.09				
C_2	3.38	4.37			0.76	0.06				
C_3	1.23	4.30			0.54	0.05				
C_4	0.05	0,41			0,16	0.03				
C_5	0.01	0.20			0.20	0.04				
Light Oil	0.62	2.20			3.76	5.31	0.05	0.74		
Wash Solvent					7.70	36.18	10.87	120.33		0.03
Process Solvent					82.50	673.33	4.82	36.65		
SRC						475.01	29.25			
Coal							64.27			
Ash/Slag							83.00			
Precoat							5.5			
H_2O/Steam				0.17	4.52	0.96			1.68	
Ammonia										
H_2S										
Total	74.99	34.92	21.58	0.17	111.61	1191.34	197.76	157.72	1.68	0.03

TABLE 6-4 (Cont'd)

Stream No.	25	26	27	28	29 & 35	30 & 31	34	36	37
Hydrogen					2.30	0.05			
CO					0.40	0.02			
CO_2					2.56	0.07			
H_2S					6.78	0.09			
O_2									
N_2					3.31	0.05			
C_1					4.67	0.09			
C_2					1.89	0.06			
C_3					1.92	0.05			
C_4					0.90	0.03			
C_5					1.20	0.04			
Light Oil	1.46		0.05	2.8	1.58	5.19			19.45
Wash Solvent	144.65		5.40		0.17	35.44			
Process Solvent	1.3		0.05		0.06	668.28	6.9		
SRC									
Coal									
Ash/Slag									
Precoat		5.5							
H_2O/Steam					1.52	0.94		3.94	
Ammonia									
H_2S									
Total	147.41	5.5	5.5	2.8	29.26	710.40	6.9	3.94	19.45

TABLE 6-4 (Cont'd)

Stream No.	39	41 & 44	42	43	46	47	48	49	51 & 56
Hydrogen									
CO									0.008
CO_2									21.93
H_2S									12.94
O_2						110.34			
N_2									
C_1									
C_2									
C_3									
C_4									
C_5									
Light Oil	0.49		0.12					0.01	
Wash Solvent	49.9		0.69	0.05				0.31	
Process Solvent	0.44		0.05	5.00				0.01	
SRC				475.01					
Coal									
Ash/Slag							122.39		
Precoat									
H_2O/Steam		27.6	0.36		46.00				1.35
Ammonia									0.01
H_2S									0.02
Total	50.83	27.6	1.22	480.06	46.00	110.34	122.39	0.33	36.26

TABLE 6-4 (Cont'd)

Stream No.	53	55	59
Hydrogen		0.11	3.29
CO		0.01	0.01
CO_2		286.4	
H_2S			
O_2			
N_2			0.15
C_1			4.01
C_2			0.04
C_3			
C_4			
C_5			
Light Oil	3.78		
Wash Solvent	0.08		
Process Solvent	0.06		
SRC			
Coal			
Ash/Slag			
Precoat			
H_2O/Steam			
Ammonia			
H_2S			
Total	3.92	286.52	7.50

Auxiliary facilities required for the plant are the following:

- Air separation plant
  (to supply oxygen to the K-T gasification process);
- Power and steam generation;
- Cooling towers; and
- Water treatment

Control/disposal modules will be required for gaseous, liquid and solid wastes.

Waste Characteristics and Comparisons

Gaseous Wastes--

The various gaseous waste stream sources are the following:

Module	Stream Nos. in Figure 6-2
Solvent recovery	29 and 35
Hydrogen recovery	15
Precoating and filtration	24
Product recovery and solidification	42
Hydrogen manufacturing	51 and 56

Table 6-5 gives the flow rates and compositions of the above waste streams. Streams 15, 29, 35, 51 and 56 have sufficient sulfur for recovery. Sulfur recovery modules are not included in this section.

The off-gases from the SRC plant, Streams 15, 29, and 35 contain large amounts of hydrocarbons in addition to the sour gases. Thus, a chemical type acid gas removal process (e.g., carbonate type) which is very common in the coke oven industry, could be used to concentrate the sour gases; and followed by a Claus process, together would recover sulfur from the concentrated sour gas stream.

Streams 24 and 42 containing small amounts of hydrocarbons should be incinerated.

TABLE 6-5. SUMMARY OF GASEOUS WASTE STREAMS, TONS/HR (BEFORE TREATMENT)

Stream No.	15	24	29	35	42	51	56
Hydrogen	1.17		0.27	2.03			
CO	0.12		0.03	0.37		0.006	0.002
CO_2	3.14		0.94	1.62		16.09	5.84
H_2S	7.99		4.46	2.32		11.62	1.32
N_2	0.23			3.31			
C_1	10.79		1.73	2.94			
C_2	4.37		1.00	0.89			
C_3	4.30		1.13	.79			
C_4	0.41		0.41	0.49			
C_5	0.20		0.33	0.87			
Light Oil	2.20		0.12	1.46	0.12		
Wash Solvent		0.03	0.07	0.10	0.69		
Process Solvent			0.06		0.05		
SRC							
Coal							
Ash/Slag							
Precoat							
H_2O/Steam				1.52	0.36	1.35	
Ammonia						0.01	
HCN						0.02	
Total	34.92	0.03	10.07	18.71	1.22	29.10	7.16

Liquid and Solid Wastes--

Process wastewater originates from both the basic SRC plant and the hydrogen generation plant. About 310 gpm of process wastewater from the SRC plant are discharged from the following modules:

Module	Stream No. in Figure 6-2
Slurry preparation, preheating and dissolving	5 and 12
Hydrogen recovery	17
Precoating and filtration	23
Solvent recovery	36
Product recovery and solidification	41 and 44

About 150 gpm of process wastewater will be discharged from the Hydrogen Manufacturing Plant, contributed mainly by Stream Nos. 88 and 89.

Table 6-6 summarizes the flow rate and compositions of all liquid waste streams from the plant.

About 122 tons per hour of solid wastes will be discharged from the plant, all originating from the Hydrogen Manufacturing Module (Stream No. 48). The above solid wastes will contain about 25 percent moisture.

The SRC plant wastewater, shown in Table 6-6, is quite similar to coke oven wastewater. It contains large quantities of phenol, ammonia, sulfide, and therefore, could be treated in a manner similarly to the coke oven wastewater treatment scheme. The wastewater from the hydrogen plant (mostly from the K-T gasification process), however, is dissimilar to the coke oven wastewater. It is a dilute stream and, therefore, no byproduct recovery type treatment is necessary.

TABLE 6-6. SUMMARY OF LIQUID WASTE STREAMS*
(BEFORE TREATMENT)

Stream No.	SRC Plant Process Waste	H_2 Plant Process Waste	Storm Runoff	Cooling Tower Blowdown	Coal Pile Runoff	Boiler Blowdown
Ammonia	0.44	0.008	0.012		0.001	
Sulfide	0.312	Trace				
Phenolics	0.351	0.004	0.006		Trace	
BOD		0.008	0.012		0.001	
Suspended Solids	0.023	Trace	0.003		0.001	
Water/Steam	78.0	37.8	57.5	287.5	68.75	102.5
COD	1.170	0.076	0.115		0.002	
Extractable Oils	0.016	0.004				
Total	80.312	37.900	57.648	287.5	68.755	102.5

* All flow rates are in tons per hour.

SECTION 7

COKE OVEN CONTROL TECHNOLOGY AND ITS APPLICABILITY TO COAL CONVERSION PROCESSES

DESULFURIZATION OF COKE OVEN GAS

In the coking operation, unacceptable quantities of hydrogen sulfide and organic sulfur compounds are formed along with the major byproduct constituent, coke oven gas. According to most government regulations, coke oven gas cannot be burned if it exceeds 15 to 50 gr/100 SCF (240 to 480 ppm by vol.) of H_2S. These regulations are summarized in Chapter 9. Since raw coke oven gas contains about 5,000 ppmv of H_2S, considerable desulfurization of the gas is, therefore, required.

Many technologies are currently employed worldwide for COG desulfurization. Table 7-1 shows the commercially available control systems and their cited efficiency ranges. All of them are of the chemical type processes rather than physical absorption type processes. These technologies are divided into three major categories: 1) Liquid Absorption Processes (e.g., Vacuum Carbonate, Sulfiban, Firma Carl Still, Diamox), 2) Wet Oxidative Processes (e.g., Stretford, Takahax, Fumaks, Giammarco Vetrocoke), and 3) Dry Oxidative Processes (Iron Oxide Boxes).

1. Liquid Absorption Processes

   Three basic steps are involved:

   a. Absorption of acid gases (H_2S, HCN, CO_2) into a recirculating solution.
   b. Stripping of acid gases from solution, and
   c. Conversion of H_2S in acid gases to either elemental sulfur or sulfuric acid.

   Absorbing Solutions:

   Vacuum Carbonate - sodium carbonate solution.
   Sulfiban - alkanolamine solution.

TABLE 7-1. COKE OVEN GAS DESULFURIZATION PROCESSES

Category	Commercial Processes	Ranges of % Sulfur Removal
Dry Oxidative	Iron-oxide boxes	90-99%
Wet Oxidative	Stretford	98-99%
	Takahax	unknown
	Rhodaks/Fumaks	unknown
	Giammarco - Vetrocoke	unknown
Liquid Absorption	Vacuum Carbonate	90-98%
	Sulfiban	90-98%
	Firma Carl/Still	90-98%
	Diamox	97%

Firma Carl Still - ammonia solution.

Diamox - ammonia solution.

2. Wet Oxidation Process

Once hydrogen sulfide is absorbed into solution, it is oxidized directly to elemental sulfur which is removed from solution by filtration.

Oxidizing Agents:

Stretford - anthraquinone disulfonic acid and sodium vanadate.

Takahax - naphthaquinone sulfonic acid.

Fumaks - ammonia and picric acid,

Giammarco Vetrocoke - alkaline arsenite and arsenate.

In each case, the oxidizing agent is regenerated by air oxidation.

3. Dry Oxidative Processing (Iron Oxide or Dry Box)

Hydrogen sulfide is adsorbed by a solid and either held as a sulfide or oxidized to elemental sulfur. Excessive labor costs and space requirements have largely eliminated the use of dry oxidative processes for new plants. A majority of the old coke oven plants use the Iron Oxide process for desulfurization.

The Iron Oxide/Dry Box process will have limited application in coal conversion processes. If applied, it will be used mostly for controlling low sulfur containing air emissions. A modified version, under laboratory scale development through DOE and EPA sponsorships, seems capable of desulfurizing acid gases at high temperatures. If this hot gas desulfurization process becomes competitive with other control processes, it could have broader applications.

Based on the desulfurization processes utilized in the coke oven industry, it appears that the Stretford process should have broad base applications in coal conversion systems. The Vacuum Carbonate and the Sulfiban process, two acid gas removal processes which have been widely employed in the U.S. for coke oven applications, should find use in the low-pressure gasification processes, or in the control of low-pressure off-gases from liquefaction processes. The physical solvent type acid gas removal processes, such as Selexol and Rectisol, have not been used for coke oven gas desulfurization because they require high-pressure feed (gas) streams. These processes, however, should have much wider application in coal conversion systems.

In the coke oven industry, the Claus process has also been used to recover sulfur from the rich acid gas stream produced from the Vacuum Carbonate and the Sulfiban processes. The Claus process has required several modifications because of the presence of hydrogen cyanide and other impurities in the acid gas feed. Since these impurities are also present in the acid gases from coal conversion systems, the Claus modifications that have been developed are of special interest because the Claus process would be a feasible sulfur recovery technology for the coal conversion systems. Discussed below are the process and design data that were available from literature sources for the various desulfurization processes which may be applicable to coal conversion systems.

Vacuum Carbonate Process

The Vacuum Carbonate process was first marketed by Koppers in the mid-1950's as an improvement over its older Seaborad process. In the Seaboard process, regeneration of the absorbing solution was accomplished by air stripping. Although this process was simple and economical it had several disadvantages. Contact with oxygen led to numerous side reactions in the solution, resulting in the need for excessive solution replacement and in salt disposal problems. The odors resulting from the foul air disposal also caused problems.

To overcome these deficiencies, the Seaboard process was modified so that the spent carbonate solution was regenerated by vacuum distillation rather than air stripping. The use of steam distillation allowed the hydrogen sulfide to be recovered in a concentrated form from which sulfuric acid or elemental sulfur could be produced.

Chemical Reactions--

$$Na_2CO_3 + H_2S \longrightarrow NaHS + NaHCO_3$$
$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$$
$$Na_2CO_3 + HCN \longrightarrow NaCN + NaHCO_3$$

The introduction of oxygen, either as the result of its presence in the coke oven gas or by air leakage into the system, results in several side reactions that produce non-regenerable salts:

$$2NaHS + 2O_2 \longrightarrow Na_2S_2O_3 + H_2O$$
$$Na_2S_2O_3 + NaCN \longrightarrow Na_2SO_3 + NaCNS$$

$$4Na_2SO_3 + 2NaHs + H_2O \longrightarrow 3Na_2S_2O_3 + 4NaOH$$

$$2NaOH + H_2S \longrightarrow Na_2S + 2H_2O$$

Process Description--

Gas is contacted counter-currently with a 3 to 3.5 percent solution of sodium carbonate in an absorber tower to remove the H_2S and other impurities such as HCN and CO_2 (See Figure 7-1). The foul solution from the base of the absorber is circulated over the actifier, where the H_2S is removed by counter-current stripping from the base of the actifier through a cooler to the absorber to complete the cycle. Typical acid gas from an actifier contains 65 to 75 percent H_2S, 10 to 15 percent CO_2, 6 to 9 percent HCN. Where closed loop final coolers are used to process COG, HCN can exceed 20 percent.

Traditionally, the Vacuum Carbonate process was designed as a single stage unit with an 80 to 90 percent hydrogen sulfide removal efficiency (93 percent maximum). However, a recent redesign of the process to a two-stage system in both the absorber and the actifier increases the overall efficiency of the process to 98 percent.

In this redesigned process, the raw coke oven gas is scrubbed of hydrogen sulfide in a two-stage packed absorber by a counter-current flow of sodium carbonate solution. The foul solution is pumped from the absorber to a two-stage actifier (regenerator), where steam stripping is used. To minimize steam consumption, stripping is carried out at 4.4 inches of mercury absolute and 54°C. Separate carbonate solution loops are maintained in each stage. However, a one-stage vapor flow is maintained in the actifier tower. The carbonate solution that contacts the inlet raw coke oven gas (and is, thus, richest in hydrogen sulfide) is sent to the upper stage of the actifier, while the solution from the upper stage of the absorber is stripped in the lower, or secondary stage, of the actifier. Solutions are circulated at a rate such as to give maximum cleaning in the second stage of the absorber. A 90 percent hydrogen sulfide removal is claimed in the first stage, with an additional 8 to 9 percent cleaning in the second.

The stripped gases and steam pass from the actifier to the vapor condenser under vacuum, and the bulk of the steam is condensed. The remaining vapors then pass through a series of steam jet ejectors and intercondensers and,

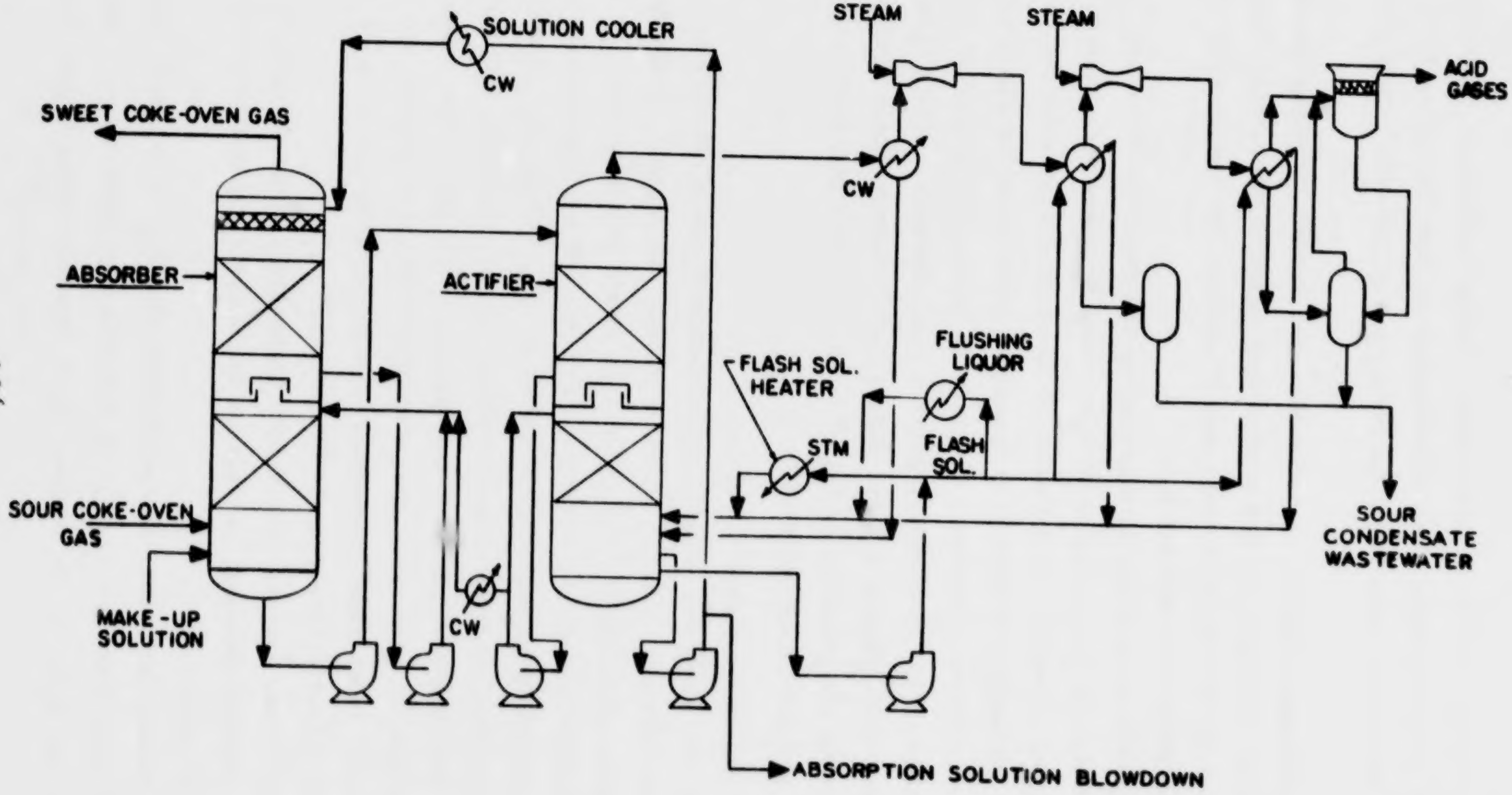

SOLUTION COOLER
CW
STEAM
STEAM
ACID GASES
SWEET COKE-OVEN GAS
CW
ABSORBER
ACTIFIER
FLUSHING LIQUOR
FLASH SOL. HEATER
STM
FLASH SOL.
SOUR COKE-OVEN GAS
MAKE-UP SOLUTION
CW
SOUR CONDENSATE WASTEWATER
ABSORPTION SOLUTION BLOWDOWN

Figure 7-1. Two stage Vacuum Carbonate system flow diagram.

finally, on to the sulfur recovery unit. Energy economy is achieved by a system that recovers waste heat and converts it into stripping steam for the actifier. Operating costs equal to those of a 93 percent removal plant are claimed.

Waste Streams--Figure 7-1 shows that the Vacuum Carbonate process produces two wastewater streams: 1) spent absorbing solution containing large amounts of suspended and dissolved solids; and 2) ejector jet condensates containing significant amounts of HCN and H_2S.

The absorbing solution is degraded by the reaction of oxygen, cyanide and perhaps ammonia in the presence of H_2S. Some of these side reactions were shown earlier. Complete replacement of spent absorbing solution is necessary after 8 to 36 months of operation (based on a few existing plant experiences).

The ejector jet condensate quantity is about 55,400 gal/day for a 60 MM SCFD desulfurization plant (9.72 gal/ton coal charged). Since this contaminated stream will contain H_2S and HCN, it will require steam stripping. Stripped gases can be recycled back to the coke oven gas feed to the Vacuum Carbonate process or incinerated.

Economics and Applications--

Table 7-2 shows the utility requirements for a 20 MM SCFD and a 60 MM SCFD Vacuum Carbonate plant. Table 7-3 gives the capital equipment costs at two different efficiencies for the plants shown in Table 7-2.

Carbonate type desulfurization processes are most applicable to gas streams containing an appreciable amount of CO_2. If H_2S is present, with little CO_2, then carbonate type processes are not suitable for desulfurization.

For many applications with gas streams containing large amounts of CO_2, the advantages of carbonate type processes over amine systems are lower utility requirements, lower plant investment (due to elimination of major heat-exchange equipment) and effective COS and CS_2 removal.

As mentioned earlier, the Vacuum Carbonate process is similar to the obsolete Seaboard process, but allows for sorbent regeneration unlike the Seaboard process.

The Vacuum Carbonate process sorbent (Na_2CO_3) is not very soluble in water and therefore, requires large circulating liquor rates. Newer carbonate processes use K_2CO_3 as the sorbent which requires lower liquor flow rates.

TABLE 7-2 VACUUM CARBONATE REQUIREMENTS(40)

	20 MMSCFD		60 MMSCFD	
Removal Efficiency	90%	93%	90%	93%
Cooling Water, GPM	1,160	1,320	4,500	7,100
Power, KW-hr/day	1,835	1,835	5,440	7,050
Na_2CO_3(100%), lb/day	177	177	530	530
Steam Requirements, lb/hr				
Actifier and/or Ejectors	6,240	6,315	18,740	19,180
Condensate Treatment	1,120	1,120	3,380	3,380
Total	7,360	7,435	22,120	22,560
Claus Steam Credits, lb/hr				
High Pressure (150 psig)	558	577	1,674	1,730
Low Pressure (30 psig)	282	292	846	875
Total	840	869	2,520	2,605
Net Process Steam Demand lb/hr	6,520	6,566	19,550	19,955

Note: Inlet gas concentration is based on 500 grains H_2S/100 SCF.

TABLE 7-3. VACUUM CARBONATE CAPITAL COSTS(40)

	20 MMSCFD		60 MMSCFD	
Removal Efficiency	90%	93%	90%	93%
Desulfurization Installed:				
Capital Cost, $MM	1.38	1.43	2.56	2.77
Claus Sulfur Recovery:				
Installed Capital Cost, $MM	0.53	0.53	0.73	0.73
Total Installed:				
Capital Costs, $MM	1.91	1.96	3.29	3.50

NOTES: 1. Inlet gas concentration is based on 500 grains H_2S/100 SCF.

2. Cost data are based on 1974 costs.

Several versions of the potassium carbonate processes are available. The hot potassium carbonate process was previously developed by the U. S. Bureau of Mines. The Benfield and Catacarb are very similar to the hot potassium process, except that they employ a proprietary catalyst to increase the rate of absorption and stripping, thus further decreasing the circulation rates of the carbonate solution. These newer carbonate processes are being considered for desulfurization of coal conversion gases because of their better economics.

Sulfiban Desulfurization Process

The Sulfiban process is a joint development of Bethlehem Steel and Black, Sivalls and Bryson.

Although the Sulfiban process was not introduced until 1972, the use of Sulfiban absorbing solution (alkanolamines) to sweeten natural and manufactured gases had been practiced for decades. Monoethanolamine (MEA) is preferred over diethanolamine for the desulfurization of coke oven gas, since it lends itself to reclamation in a sidestream reclaimer.

Chemical Reactions--

The H_2S, HCN, organic sulfides and a portion of the CO_2 are chemically absorbed in MEA as follows:

$$RNH_2 + H_2S \rightleftarrows RNH_3HS$$

$$RNH_2 + HCN \rightleftarrows RNH_3CN$$

$$2RNH_2 + CO_2 + H_2O \rightleftarrows (RNH_3)_2CO_3$$

When heat is applied in the regenerator stripper, the above reactions are reversed, freeing the acid gas. However, reactions between MEA and organic sulfides such as COS and CS_2 are not reversible. Also, if oxygen is present in the system, an irreversible side reaction will take place between the MEA, HCN and O_2 producing amine thiocyanates and thiosulfates.

Process Description--

The Sulfiban process is operationally similar to the Vacuum Carbonate process with the single exception that the actifier operates at atmospheric pressure and about 230°F. As a result, heat must be supplied in the form of process steam (at least 30 psig).

The sour coke oven gas is contacted counter-currently (see Figure 7-2) with a 13 to 18 weight percent aqueous solution of MEA in an absorption column. The resulting foul solution is regenerated with steam in an actifier. The acid gases from the actifier typically contain 35 to 45 mole percent hydrogen sulfide, 55 to 60 mole percent carbon dioxide, and 2 to 4 mole percent hydrogen cyanide, together with fractional percentages of organic sulfur compounds (primarily carbon disulfide and carbonyl sulfide).

After counter-current contact with the coke oven gas, the fouled solution passes through a series of heat recovery exchangers on its way to the actifier. The actifier overhead, consisting primarily of water vapor and acid gas, is passed through a condenser and into an accumulator where separation of the condensables occurs. The acid gas vapors pass on to the sulfur recovery system, and the condensate is returned to the actifier as reflux.

After passing down the actifier, the MEA solution enters a steam-fired reboiler, where additional stripping occurs (primarily of carbon dioxide), and stripping steam for the actifier is generated. A sidestream from the reboiler enters a reclaimer fired by higher-pressure steam, in which the MEA is vaporized and returned to the system and the non-volatile components are removed from the circulating solution. The bulk of the reboiler effluent passes to a surge tank, from which it is returned to the absorber via the solution heat exchangers and cooler.

Sulfiban pilot plant studies have demonstrated a clear capability for COG desulfurization to H_2S concentrations of 10 grains/100 scf or less. Efficiencies range between 90 and 98 percent.

Only one liquid waste stream of consequence is produced in the Sulfiban plant; spent absorbing solution accumulates as a sludge in the actifier reboiler and must be discharged periodically. Pilot plant data indicate that about 37 gal/day of sludge containing FeS, iron ferrocyanide, thiourea, etc. will have to be removed from a plant producing 60 MM SCFD of coke oven gas.

Sulfiban operating requirements are given in Table 7-4 for 20 MM SCFD and 60 MM SCFD plants. Cost data for the plants are presented in Table 7-5.

Applications--

The Sulfiban is a basic amine process (MEA) which has been used as a standard in the gas purification/removal industry. It has been applied in the

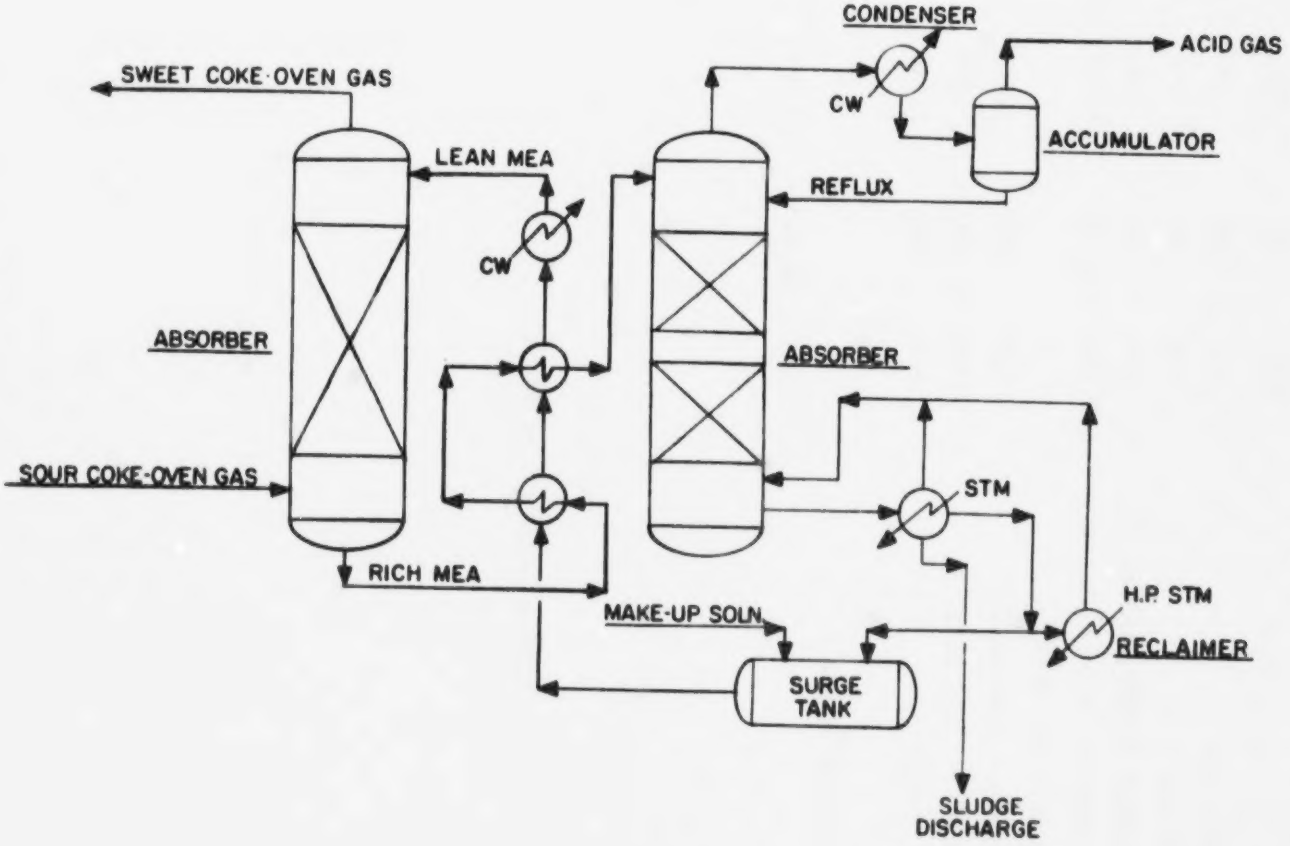

CONDENSER
ACID GAS
SWEET COKE·OVEN GAS
CW
ACCUMULATOR
LEAN MEA
REFLUX
CW
ABSORBER
ABSORBER
STM
SOUR COKE-OVEN GAS
RICH MEA
H.P. STM
MAKE-UP SOLN
RECLAIMER
SURGE
TANK
SLUDGE
DISCHARGE

Figure 7-2. Sulfiban desulfurization process.

TABLE 7-4. SULFIBAN OPERATING REQUIREMENTS(40)

	20 MMSCFD		60 MMSCFD	
Efficiency	90%	98%	90%	98%
Cooling Water, GPM	530	1,060	1,590	3,180
Power, KW-Hr/Day	1,300	1,300	4,148	4,148
Monoethanolamine (100%), lb/day	300	300	900	900
Steam Requirements, lb/hr: Actifier	5,840	10,914	17,520	32,746
Claus Steam Credits, lb/hr:				
High Pressure (150 psig)	558	607	1,674	1,824
Low Pressure (30 psig)	282	307	846	922
TOTAL	840	914	2,520	2,746
NET PROCESS STEAM DEMAND				
lb/hr	5,000	10,000	15,000	3,000

NOTE: Basis - 500 grains H_2S/100 scf at inlet.

TABLE 7-5. SULFIBAN - CAPITAL COSTS(40)

Efficiency	20 MMSCFD		60 MMSCFD	
	90%	98%	90%	98%
Desulfurization Installed:				
Capital Cost, \$MM	1.27	1.42	2.5	2.8
Claus Sulfur Recovery:				
Installed Capital Cost, \$MM	0.55	0.55	0.70	0.70
HCN Pretreatment:				
Installed Capital Cost (via catalytic decomposition), \$MM	0.20	0.20	0.25	0.25
TOTAL INSTALLED CAPITAL COSTS, \$MM	2.02	2.17	3.45	3.75

NOTES: 1. Basis - 500 grains H_2S/100 scf at inlet.

2. 1974 costs data.

desulfurization of coke oven gas, refinery gas, natural gas, and in the manufacture of synthesis gas and hydrogen (more than 100 plants have been built world wide by Black, Sivalls and Bryson).

The Sulfiban process will have applicability in the U.S. coal conversion processes especially for the removal of H_2S and CO_2 from low pressure raw product and off-gases. Since the process removes organic sulfides by irreversible chemical reactions, solvent make up is required by the process. The temperature of the feed gas has to be below 100°F.

Iron Oxide Process

The Iron Oxide or Dry Box process is one of the oldest gas treating techniques known. The process has found widespread use in some European countries where essentially complete H_2S removal is necessary and where some manufactured and synthesis gases contain impurities which react irreversibly with chemicals used in liquid purification processes. The process is usually limited to treating gases of small to medium volumes and containing 1.5 volume percent H_2S or less.

Advantages of the process are essentially complete H_2S removal, ease of operation and simplicity of installation. Disadvantages are: 1) the sulfur removed by the process cannot be recovered economically; and 2) large amounts of labor are required during periodic bed replacement and solid wastes disposal. For these reasons, the Iron Oxide process will have very limited application in coal conversion processes. Example of a possible application is the treatment of low volume sour gases produced by the byproduct upgrading plants which are remotely located from the main sulfur removal plant of the coal conversion process.

Chemical Reactions--

(1) Reaction: $2Fe_2O_3 + 6H_2S \longrightarrow 2Fe_2S_3 + 6H_2O$

(2) Regeneration: $2Fe_2S_3 + 3O_2 \longrightarrow 2Fe_2O_3 + 6S$

Overall: $6H_2S + 3O_2 \longrightarrow 6H_2O + 6S$

Process Description--

Dry Box purification is the removal of hydrogen sulfide from gas by bringing the gas into contact with iron oxide in the presence of water. The efficiency and economy of sulfur removal are dependent upon the activity, capacity and availability of the oxide used, the ease with which the gas can be passed through the bed containing the oxide, and upon certain conditions of temperature and moisture. Hydrogen sulfide removal is quite exceptional for small gas volumes; a sweetened gas of less than 0.1 grain H_2S/100 scf is easily obtained.

The process uses wood shavings impregnated with ferric oxide in hydrated form. The bed is gradually deactivated by formation of ferric sulfide and can be partially regenerated by air oxidation of the ferric sulfide to ferric oxide and sulfur. However, eventually the bed becomes plugged with sulfur and must be replaced. If a batch-type regeneration is employed, about 4 regenerations are possible before the beds of iron sponge must be changed. Two or more towers or iron oxide boxes are utilized.

In general, the sulfur is not recovered from the sponge beds. The process removes no CO_2.

There is no theoretical basis for the design procedure, but several empirical rules can be followed:

1. The tower or box should be of such a horizontal cross-section as to limit sulfur deposition to a maximum of 15 grains per square foot of bed cross-sectional area per minute.
2. The operating temperature of the bed should always be below 105°F. Otherwise, the water of crystallization in the Fe_2O_3 molecule will be driven off and the activity of the material destroyed.
3. The height of the tower or box is recommended to be at least 10 feet to produce a pressure drop sufficient for proper gas distribution over the entire cross-sectional area of the tower.
4. Sponge mixtures containing 5 to 10 lbs of Fe_2O_3 per cubic foot are satisfactory, and it is customary to figure on 6 cubic feet of sponge per 100 SCFD.
5. The sponge does not function properly if it contains less than 17 percent moisture, or more than 55 percent. A desirable moisture content is between 30 and 50 percent. The function of the water in the tower or box is to act as a differential solvent for the H_2S,

and to hold it for a sufficient time for the oxide to react with it. A further function of the water is to furnish sufficient drops to dissolve and remove from the tower or box the soluble salts formed during purification.

6. The theoretical maximum for sulfur removal per cubic foot of sponge is 5.8 pounds. This is based on 10 pounds of iron-oxide per cubic foot of sponge mixture.

Stretford Sulfur Recovery Process

The Stretford process was originally developed to overcome some of the shortcomings of earlier absorption/oxidation processes. The process is capable of reducing the H_2S content in coke oven gas to less than 10 grains/100 scf. Sulfur recovery between 98 and 99 percent is possible. The process does not remove organic sulfur, and requires pretreatment for removal of large quantities of SO_2, HCN, or heavy hydrocarbons. It produces a wastewater stream containing Stretford solution which requires treatment.

Chemical Reactions--

(1) H_2S absorption:

$$H_2S + Na_2CO_3 \longrightarrow NaHS + NaHCO_3$$

(2) Vanadium reduction and sulfur formation:

$$4NaVO_3 + 2NaHS + H_2O \longrightarrow Na_2V_4O_9 + 2S + 4NaOH$$

(3) Vanadate reoxidation with anthraquinone disulfonic acid (ADA):

$$Na_2V_4O_9 + 2NaOH\ H_2O + 2ADA \longrightarrow 4NaVO_3 + 2ADA\ (reduced)$$

(4) ADA reoxidation:

$$2ADA\ (reduced) + O_2 \longrightarrow 2ADA + 2H_2O$$

Major Side Reactions--

(1) Thiosulfate formation:

$$2NaHS + 2O_2 \longrightarrow Na_2S_2O_3 + H_2O$$

(2) Cyanide conversion to sodium thiocyanate:

$$HCN + NaHS + 1/2\ O_2 \longrightarrow NaCNS + H_2O$$

(3) Sulfur dioxide conversion to sodium sulfate:

$$2Na_2CO_3 + SO_2 + H_2O \longrightarrow Na_2SO_3 + 2NaHCO_3$$

$$Na_2SO_3 + 1/2\ O_2 \longrightarrow Na_2SO_4$$

Polysulfide Pretreatment Reactions--

(1) $(NH_4)_2S_{x+1} + HCN + NH_3 \longrightarrow NH_4SCN + (NH_4)_2S_x$

(2) $(NH_4)_2S_x + S \longrightarrow (NH_4)_2S_{x+1}$

Process Description--

The raw coke oven gas (COG) is first pretreated to remove hydrogen cyanide in a counter-current absorber with a solution of ammonium or sodium polysulfide. The polysulfide reacts with the hydrogen cyanide in the coke oven gas to form thiocyanate. The spent polysulfide is regenerated by the reaction of the wash solution with elemental sulfur (see pretreatment reactions above). Fresh polysulfide solution is continually added to the wash solution, and a purge stream of the spent wash solution is sent to waste treatment. The cyanide absorber can have an efficiency of between 90 to 97 percent.

The cyanide-free COG is then scrubbed (see Figure 7-3) in an absorber by counter-current washing with an aqueous solution of sodium carbonate, anthraquinone disulfonic acid (ADA), citric acid, and sodium meta-vanadate. The hydrogen sulfide initially dissolves in the wash solution and is then rapidly oxidized by the vanadate ion to elemental sulfur. The vanadate ion is reduced to the vanadous state, which is returned to its original form by the ADA. The now sweetened COG passes into the distribution system.

Underneath the absorber there is a delay (reaction) tank where a liquid residence time of 10 to 20 minutes is maintained to allow complete conversion of the hydrosulfide to elemental sulfur.

The spent solution passes into an oxidizer, where air (up to 400 percent excess) is bubbled through the solution to reoxidize the ADA. The rising air bubbles also carry the suspended sulfur particles to the surface, where they form a froth (6 to 8 percent sulfur) which is skimmed off. Underflow goes to a surge tank and is eventually recycled to the H_2S absorber. A purge stream containing contaminated Stretford solution is withdrawn from the surge tank and sent to waste treatment.

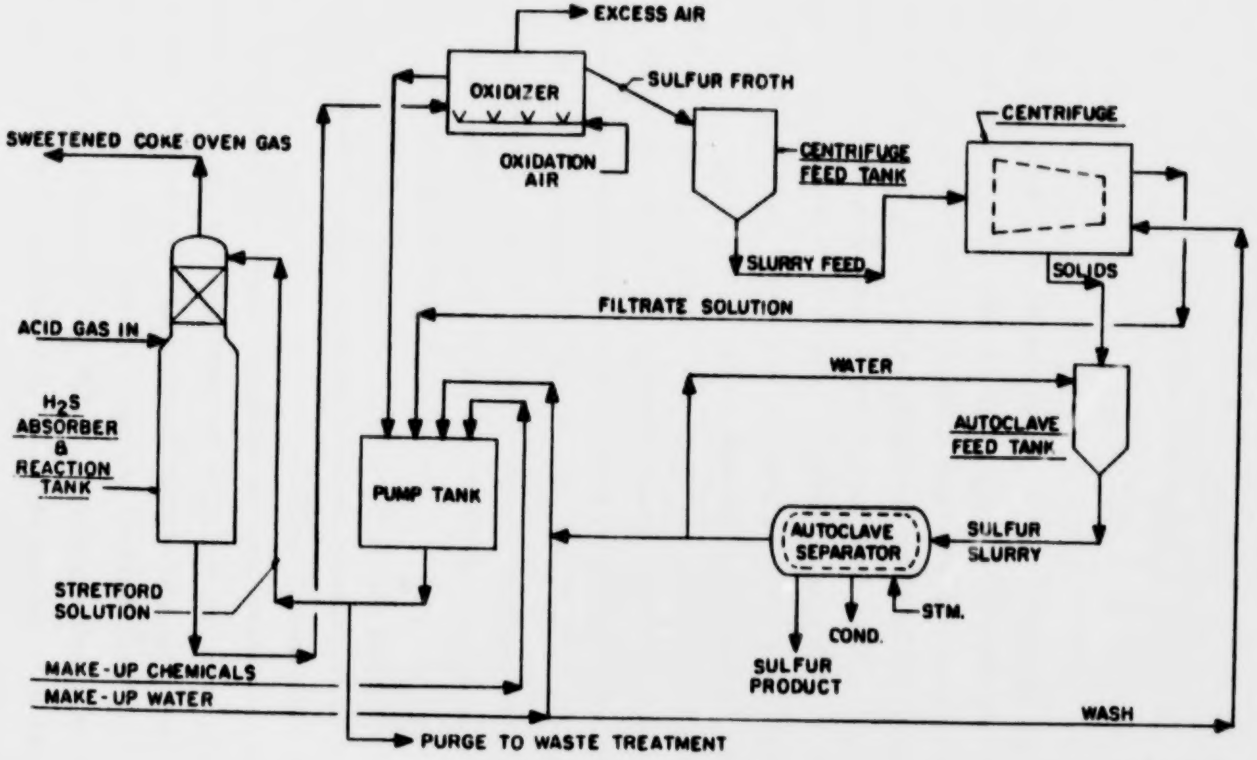

EXCESS AIR
OXIDIZER
SULFUR FROTH
OXIDATION AIR
CENTRIFUGE
SWEETENED COKE OVEN GAS
CENTRIFUGE FEED TANK
SLURRY FEED
SOLIDS
FILTRATE SOLUTION
ACID GAS IN
WATER
H2S ABSORBER & REACTION TANK
AUTOCLAVE FEED TANK
PUMP TANK
AUTOCLAVE SEPARATOR
SULFUR SLURRY
STRETFORD SOLUTION
STM.
COND.
MAKE-UP CHEMICALS
SULFUR PRODUCT
MAKE-UP WATER
WASH
PURGE TO WASTE TREATMENT

Figure 7-3. Stretford sulfur recovery process flow diagram.

Sulfur Recovery--A number of methods are available for handling the sulfur froth. Some of the alternative sulfur recovery methods, and the final product form, are:

1. Filtration, yielding sulfur cake;
2. Centrifugation, yielding sulfur cake;
3. Filtration or centrifugation followed by autoclaving and separation, yielding high purity molten sulfur; and
4. Filtration or centrifugation followed by direct injection steam melting and separation, yielding high purity molten sulfur.

When sulfur is to be recovered by filtration, a rotary vacuum drum filter is generally used. The filter cake produced contains 50 to 60 percent solids. One or more wash cycles are employed to remove solution components from the cake. The filtrate and wash are collected and returned to the system.

Continuous centrifuges may be employed for higher throughput. Again, the filtrate and wash are returned to the system for reuse of valuable components in the liquor.

Sulfur cake, or sulfur cake reslurried in water, can be fed to an autoclave melter-separator. The melter-separator is a vessel with a jacket or internal coil that is heated by steam at about 40 psig. Sulfur melts (at the operating conditions of 25 psig and 266°F) and is separated from the aqueous layer containing the Stretford solution components. The molten sulfur is pumped to storage and recovered liquor is returned to the system. It has been reported that part of the ADA that enters the autoclave is desulfonated at the elevated temperatures to 2,7-dihydroxyanthraquinone. This compound must then be separated and purged from the system.

Direct injection sulfur melting is similar to that described above except that steam is used directly rather than indirect coil or jacket heating.

Sulfur recovered by any of the above methods should be of a typical purity of 99.5 percent or better.

Stretford Process Wastewater Treatment--

Treatment of Polysulfide Pretreatment Purge Stream--The purge stream from the polysulfide pretreatment contains large concentrations of thiocyanate, polysulfide, ammonia, sulfide and elemental sulfur. Two processes have been investigated with success on a laboratory scale for the treatment of these wastes: (1) combustion and (2) decomposition.

When combustion is performed in an excess of air, sodium sulfate is formed as a combustion product; whereas with a deficiency of air, sodium sulfide and sodium sulfite are formed. If sufficient sodium is not present in the aqueous waste, caustic must be added to the feed stream.

The Ralph M. Parsons Co. has developed a process to decompose the polysulfide process wastes by catalytic hydrogenation. The process converts the wastes to NH_3, H_2S and CO which can be returned to the coke oven gas stream. No large treatment plant has been built based on this process.

Treatment of Stretford Purge Stream--The contaminated Stretford solution purge stream contains large amounts of pollutants similar to the polysulfide pretreatment waste. It has been treated according to the following three methods:

1. Combustion,
2. High temperature hydrolysis, and
3. Carbon adsorption followed by ion exchange.

The combustion disposal method is essentially the same as that described above for the treatment of polysulfide pretreatment wastes. Although combustion is effective, the other two methods are potentially attractive since costly reagents can be recovered and recycled to the process.

The high temperature hydrolysis process has been developed by Woodall Duckham Limited. In this process, both the Stretford purge stream and the polysulfide pretreatment waste can be treated to recover vanadium, sodium carbonate, and some sodium sulfide and sulfate; and to break down all of the thiocyanate and most of the thiosulfate in the effluent.

In the Woodall Duckham process the wastewater is first concentrated in an evaporator. The concentrated solution is next fed to a high-temperature hydrolyzer where the solution is evaporated to dryness and decomposed in a reducing environment. The reducing atmosphere is produced by combustion of fuel, e.g., coke oven gas. Gases leaving the hydrolyzer are cleaned of solids in cyclones and then fed to the Stretford absorber. The solids recovered from the cyclones, containing vanadium and sodium salts, are dissolved and recycled to the Stretford plant.

A U.S. patent was issued in May, 1974 to the North Western Gas Board for a process to recover ADA and vanadium salt from Stretford waste liquor(45).

The process uses carbon adsorption and ion exchange to selectively remove ADA and vanadium salts, respectively. The materials are recovered upon regeneration of the beds. It is not known if the process has been tried commercially.

In the process, the Stretford effluent, adjusted to a pH in the range of 2.5 to 3, is passed through an adsorbent bed containing activated carbon. ADA and dihydroxyanthraquinone are adsorbed and retained in the bed. The solution then enters an ion exchange bed where vanadium compounds are removed. In the above mentioned pH range, an anion exchange resin of the modified polystyrene type is reported to be suitable.

The activated carbon and the anion exchange resin may be regenerated for reuse. This is achieved in the case of the carbon by washing the bed with hot water, dilute sodium hydroxide or alkaline sodium dithionite. This removes the adsorbed anthraquinone compounds from the bed. ADA is separated from the dihydroxyanthraquinone and recycled back to the process. The dihydroxyanthraquinone is discarded.

Regeneration of the ion exchange resin is accomplished by passing sodium hydroxide through the bed. Vanadate ion is eluted from the bed as sodium vanadate and returned to the Stretford plant.

Economics and Applications--

Capital and operating costs for the Stretford process are affected by many variables. These include: inlet gas composition, operating pressure, outlet gas purity, pretreatment and waste treatment requirements. Generalized economic analyses, therefore, can be misleading.

Table 7-6 presents cost data for 20 MM SCFD and 60 MM SCFD coke oven gas plants. A 5,000 TPD coal-fired low-Btu gas production facility burning 2 percent (by wt) sulfur with a gas volume of 60,000 SCFM is operated by Combustion Engineering in Windsor, Conn., and utilizes Stretford capital equipment estimated to cost three million dollars (1978 costs).

Major applications of the Stretford process include the desulfurization of: refinery and petrochemical off-gases, coke oven gas, flexicoking fuel gas, Claus tail gas, fluidized bed combustion of coal and coal gasification/liquefaction off-gases. Currently, over 50 plants are utilizing the Stretford process including several coal conversion plants. The process is operating in a commercial coal conversion plant in Sasol, South Africa. Several developing

TABLE 7-6. STRETFORD DESULFURIZATION - CAPITAL & OPERATING COSTS(40)

ITEM	(W/O HCN or Effluent Treatment) 20 MMSCFD	60 MMSCFD	60 MMSCFD*
Operating Costs			
Power, 1.4c/KWHR	$64.60	$186.20	$252.00
Cool. H_2O, 12c/M Gal			2.16
Steam $1.50/M lb	43.20	95.04	237.60
Chemical Makeup, $/day	53.36	150.08	668.28
Total Installed Capital Costs			
$ MM	1.45	2.88	3.45

* Integrated system includes Woodall-Duckham wastewater effluent treatment and no polysulfide pretreatment equipment.

NOTE: Basis - 500 grain H_2S/100 SCF.

coal conversion processes are also employing it. They are: the Synthane pilot plant at the Pittsburgh Energy Research Center; the Combustion Engineering low Btu gasification facility in Windsor, Conn.; the SRC pilot plant at Tacoma, Washington; and the DOE-owned Cresap test facility. Several Lurgi based commercial coal gasification plants under design conditions in the U.S. (e.g., El Paso and WESCO plants) have utilized Stretford to remove H_2S from Claus tail gas and low-H_2S containing off-gas from the Rectisol acid gas removal process. The Stretford process is suitable for gas streams with low H_2S (less than 15 percent) concentrations.

Claus Sulfur Recovery Process

The Claus process has been used in several coke oven plants to recover elemental sulfur from the coke oven gases. Operating experiences of three Bethlehem Steel Corporation plants were recently published(34). It was found that certain process modifications were necessary due to the effect of chemical components present in the coke oven gas which are not typical of the Claus plant application for petroleum derived gases. The constituents are hydrogen cyanide, tar, naphthalene, hydrocarbons, organic sulfur, etc. Since these components are also present in the coal conversion acid gases, Claus plant experiences from the coke oven application could be useful.

Elemental sulfur is produced in the process by the Claus reaction between hydrogen sulfide and sulfur dioxide which yields sulfur and water, as follows:

$$2H_2S + SO_2 \overset{Cat}{\rightleftarrows} 3S + 2H_2O$$

The SO_2 is supplied either by burning one-third of the H_2S-containing acid gas in a slip-stream and recombining the gases, or by reacting the total acid gas with a limited amount of air. When the acid gas feed to the Claus plant is a lean stream, i.e., 25 to 35 vol percent H_2S in the feed, the slip-stream scheme is favored. For rich acid gas feed, the latter technique is more cost effective. (Note: Most of the Claus plants in the coke oven industry follow this technique.)

Figure 7-4 shows a flow diagram of a typical Claus plant in the coke oven industry. The plant consists of:

1. A furnace section where the SO_2 reactants are produced by burning the H_2S-containing feed gas. Also, a substantial amount of sulfur is formed in this section by non-catalytic reaction of hydrogen sulfide and sulfur dioxide.

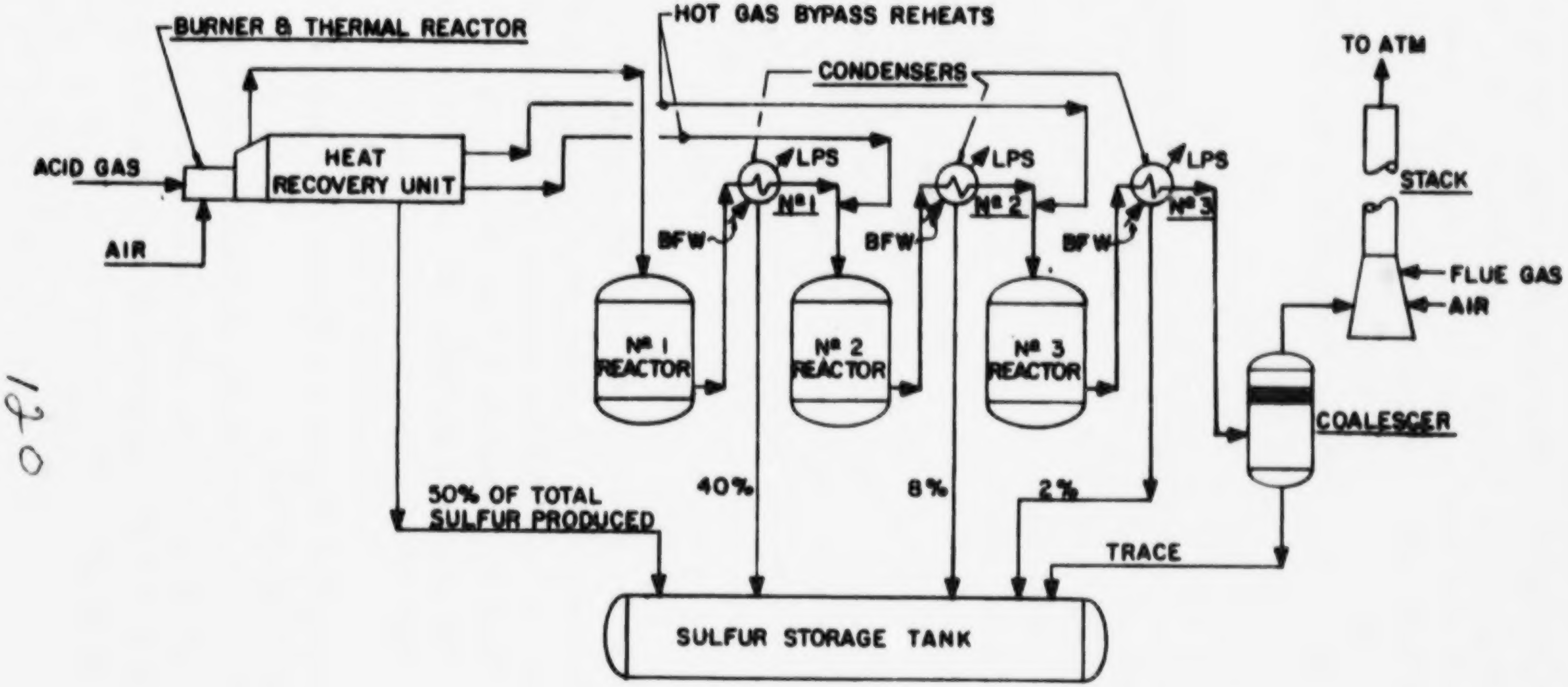

BURNER & THERMAL REACTOR
HOT GAS BYPASS REHEATS
CONDENSERS
TO ATM
ACID GAS
AIR
HEAT RECOVERY UNIT
LPS
LPS
LPS
Nº 1
Nº 2
Nº 3
BFW
BFW
BFW
STACK
FLUE GAS
AIR
Nº 1 REACTOR
Nº 2 REACTOR
Nº 3 REACTOR
COALESCER
50% OF TOTAL SULFUR PRODUCED
40%
8%
2%
TRACE
SULFUR STORAGE TANK

Figure 7-4. Claus sulfur recovery process.

2. A series of catalytic reaction zones where the Claus reaction proceeds to a further degree of completion. This section consists of a repetition of three basic steps: reaction, cooling and condensing of sulfur, and reheating of gas going to the next reactor.

Typical compositions of acid gas feeds (produced by Vacuum Carbonate systems) to the three Claus plants operating at Bethlehem Steel coke oven plants are shown in Table 7-7. Using these rich feed streams and a Claus process that contains a furnace section and three catalytic converter steps, the Bethlehem Steel experience has demonstrated sulfur recovery efficiencies of 95 to 96 percent.

Approximately 50 percent of the total sulfur production occurs in the thermal section (furnace and waste heat recovery); sulfur made in the three reactor/condenser passes is 40 percent, 8 percent and 2 percent of the total production, respectively.

The tail gas quantity from the above process is approximately 1.77 times the volumetric flow rate of the acid gas feed. Substantial amounts of sulfur compounds will be present in the tail gas, e.g., 2,200 ppmv of H_2S, 1,500 ppmv of COS, 1,300 ppmv of SO_2 and 100 ppmv of CS_2. Therefore, the tail gas is incinerated to convert more odorous and toxic sulfur compounds to SO_2, before discharge to the atmosphere. Other types of tail gas control systems do not appear to be used in the coke oven industry according to our literature review.

The organic sulfur compounds in the tail gas originate from many side reactions in the Claus process involving carbon dioxide, hydrocarbons, carbon monoxide, hydrogen sulfide and sulfur dioxides. Some of these reactions are given below:

$$CO_2 + H_2S \rightleftharpoons COS + H_2O$$

$$CO + 1/2\ S_2 \rightleftharpoons COS$$

$$CH_4 + SO_2 \rightleftharpoons COS + H_2O + H_2$$

$$CS_2 + H_2O \rightleftharpoons COS + H_2S$$

$$CH_4 + 2S_2 \leftrightharpoons CS_2 + H_2S$$

Increasing the CO_2 and hydrocarbons present in the feed gas to the Claus unit, will increase the amount of COS and CS_2 present in the tail gas. The effect

TABLE 7-7. TYPICAL CLAUS PLANT FEED COMPOSITION FOR THE COKE INDUSTRY(34)

Component	Composition in Vol %		
	Plant A	Plant B	Plant C
Hydrogen sulfide	69.20	78.97	77.82
Carbon dioxide	8.28	15.43	9.71
Hydrogen cyanide	19.99	0.35	7.71
Carbon disulfide	0.04	0.48	0.29
Sulfur dioxide	0.02	0.08	0.09
Toluene	0.11	0.03	0.05
Benzene	0.83	0.11	0.05
Ethylene	-	0.50	0.41
Methane	0.33	1.91	0.68
Oxygen	-	-	0.29
Nitrogen	0.17	2.04	2.81
Argon	0.28	0.04	0.09
Water	0.85	0.06	-

of the above impurities is more pronounced when the Claus feed gas is a lean stream (less than 35 percent H_2S).

Effect of Hydrogen Cyanide--

The hydrogen cyanide in the acid gas feed to the Claus unit was found to cause severe corrosion of the burner, sulfur separator vessel and sulfur line. Analysis of the corrosion products showed that they contained large amounts of thiocyanates.

To eliminate the hydrogen cyanide from the acid gas feed to the Claus unit, Bethlehem Steel has successfully applied a catalytic oxidation reactor (cyanide destruct reactor). The reactor uses Claus type catalyst at a temperature of approximately 500 to 600°F. Cyanides are destroyed according to the following:

$$HCN + H_2O \longrightarrow NH_3 + CO$$

$$HCN + 2H_2S + 1/2\ O_2 \longrightarrow CS_2 + NH_3 + H_2O$$

The above system oxidizes 95 percent of the cyanide present in the acid gas feeding the Claus plant, thereby eliminating the previous corrosion problems.

Other systems that have been examined for removing hydrogen cyanide from the acid gas feed streams are:

1. Water washing (scrubbing), Bethlehem Steel,
2. Improved Claus combustion methods, Koppers, and
3. Catalytic hydrolysis, the North Western Gas Board, U.K.

Water washing worked but required higher capital cost than the catalytic oxidation process. Modified Claus combustion requires a slightly air-rich condition during Claus combustion, resulting in lower sulfur yields. Catalytic hydrolysis process encountered catalyst fouling with the small amounts of tars present in the acid gas feed.

Economics and Applications--

The capital cost of a Claus plant depends on many factors such as: the concentration of H_2S in the gas; the removal efficiencies (number of converter stages); and the concentration of impurities such as hydrocarbons, cyanides and ammonia. Costs for coke oven applications (inlet gas concentration of 500 grains per 100 SCF) are given, for two sizes (20 MM SCFD and 60 MMSCFD), in Tables 7-3 and 7-5. For the larger plant, which will recover about 20 ton/day of sulfur, the capital cost is about $730,000 (1974 costs).

For a Claus sulfur recovery plant needed to recover about 560 ton/day of sulfur from a 20,000 TPD SRC-I process discussed in Section 6, it was estimated that the capital cost would be approximately six million dollars (1976 costs). The cost would be about fourteen million dollars with a tail gas unit (SCOT process) which is needed to meet air pollution control standards.

The Claus process has been used commercially for sulfur recovery from refinery, coke oven and natural gases. Although it has not been used in any of the existing commercial coal gasification plants, it is included in the design of a number of proposed commercial gasification and liquefaction plants for gas streams with high H_2S (more than 15 percent). The Claus process has been used with a number of developing gasification processes, e.g. Hygas, Bigas and the Lurgi installation at Westfield, Scotland.

WASTEWATER CONTROL TECHNOLOGY

In Section 4, the principal sources of Byproduct coke plant wastewaters were identified as ammonia liquor blowdown, final cooler blowdown, light oil plant (also called benzol) wastewater and coal pile runoff. Characteristics of these wastewaters and their counterparts in the coal conversion systems were discussed in Section 4, 5 and 6. Since the first three process wastewater streams come in contact with coke oven gases, they contain large amounts of the following pollutants: phenol, ammonia, cyanide, thiocyanate, sulfides, etc. The ammonia liquor blowdown stream has the largest concentration of these and other pollutants.

Various treatment schemes for these streams are used in the coke oven industry. A summary of the important control/disposal methods is given below:

Light Oil Plant and Final Cooler Wastewaters--Although these streams contain large amounts of phenol, ammonia and cyanide, a majority of the plants send these streams to coke quenching without any treatment. (Note: It may be construed that similar practices would not be permitted in the coal conversion processes in analogous situations; e.g. ash quenching with dirty process wastewater.) A few plants treat these streams similar to the ammonia liquor blowdown before re-use or discharge to the receiving stream.

Coal Pile Runoff--A majority of the plants have some kind of control technology to recover fine coal particles from the runoff. Since there are no existing effluent limitations on storm water runoff from the coal pile, no other treatment technology is used. The EPA, however, has proposed suspended solids concentration and pH limitations that may be effective in 1983. Should these limitations become effective, better settling systems (e.g., with flocculating chemical addition chambers, and clarification vessels) and pH controlling vessels will be required.

Ammonia Liquor Blowdown--Most plants keep this stream segregated from other low strength wastewaters and treat it extensively before discharge to the receiving stream. Phenols and ammonia are removed from the wastewater by various means. Steam stripping of ammonia, biological oxidation and/or solvent extraction of the phenolics and organics are very common treatment technologies.

Figure 7-5 presents currently employed treatment practices at five coke oven plants. All the plants perform extensive treatment of the ammonia liquor blowdown before discharge to the receiving stream. The treatment schemes, however, vary significantly among the different plants. With the exception of Plant E, all the plants recycle the final cooler and the benzol plant (light oil) wastewaters to coke quenching. Plant E uses complete physical/chemical treatment for the ammonia liquor blowdown, final cooler, and benzol plant wastewaters; carbon adsorption is the significant unit operation in the treatment scheme. Summary features of the treatment plants are given below:

Plant A--Waste ammonia liquor, light oil wastewaters and final cooler wastewaters are treated first in a free-leg ammonia still (fixed ammonia not removed), and subsequently, with a proprietary solvent extraction process for phenol removal before discharge to receiving stream.

Plant B--Waste ammonia liquor, after dilution with non-contact cooling water, is treated via the activated sludge system and clarification, followed by discharge to the receiving stream. Final cooler and benzol plant wastewaters are sent to coke quenching for complete evaporation.

Plant C--Waste ammonia liquor is treated via solvent extraction of phenol followed by ammonia stripping (fixed ammonia released by lime treatment) before discharge to a municipal facility. Final cooler and light oil wastewaters are sent to coke quenching for complete evaporation.

Plant D--Waste ammonia liquor is first treated in a stripping tower for H_2S removal; next, phenol is removed by solvent extraction; and, finally, ammonia is removed by steam stripping (fixed ammonia released by lime treatment).

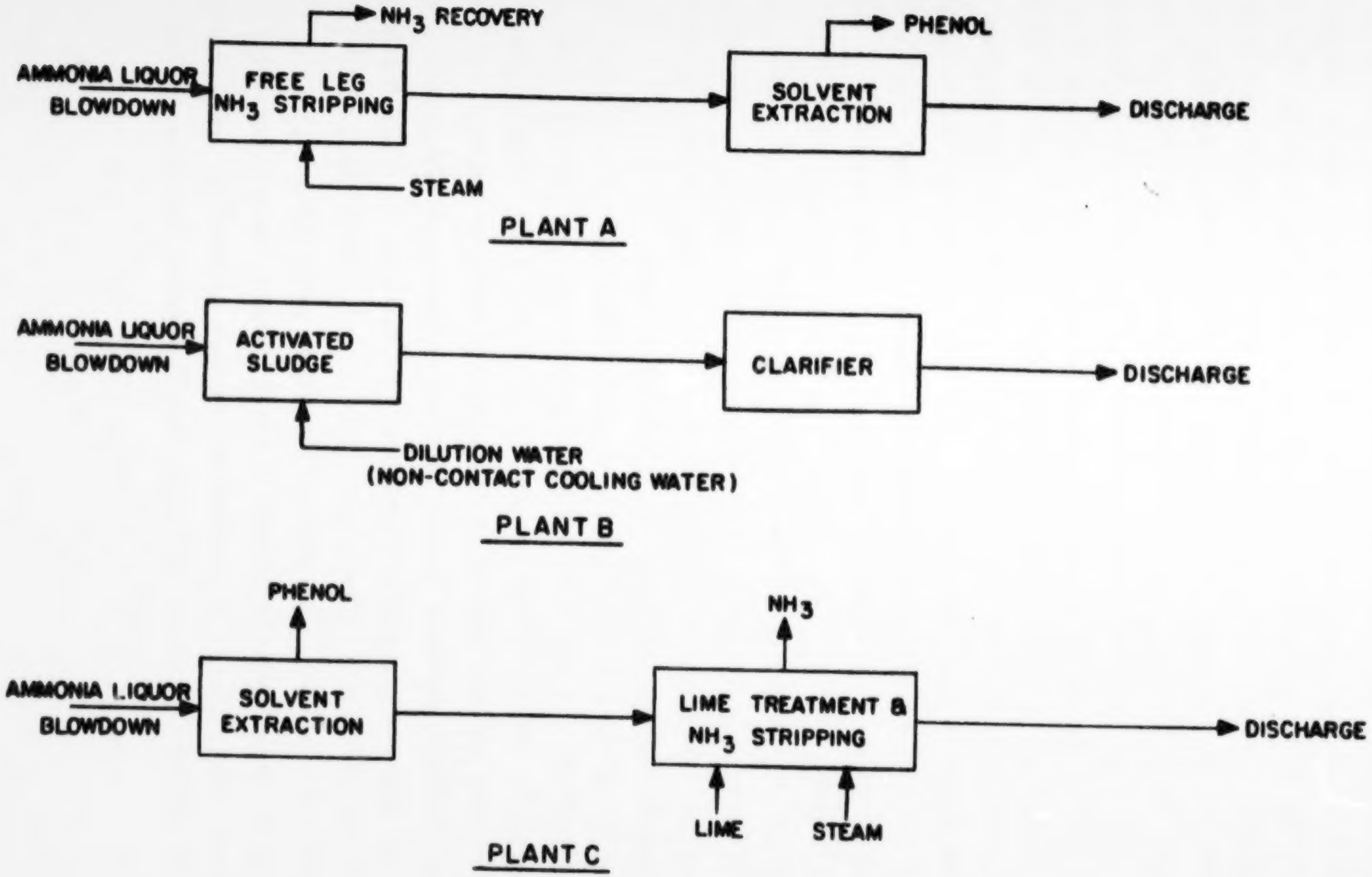

AMMONIA LIQUOR
BLOWDOWN
FREE LEG
NH_3 STRIPPING
NH_3 RECOVERY
STEAM
SOLVENT
EXTRACTION
PHENOL
DISCHARGE
PLANT A
AMMONIA LIQUOR
BLOWDOWN
ACTIVATED
SLUDGE
DILUTION WATER
(NON-CONTACT COOLING WATER)
CLARIFIER
DISCHARGE
PLANT B
AMMONIA LIQUOR
BLOWDOWN
SOLVENT
EXTRACTION
PHENOL
LIME TREATMENT &
NH_3 STRIPPING
NH_3
LIME
STEAM
DISCHARGE
PLANT C

Figure 7-5 (Pg. 1 of 2). Coke plant wastewater treatment systems.

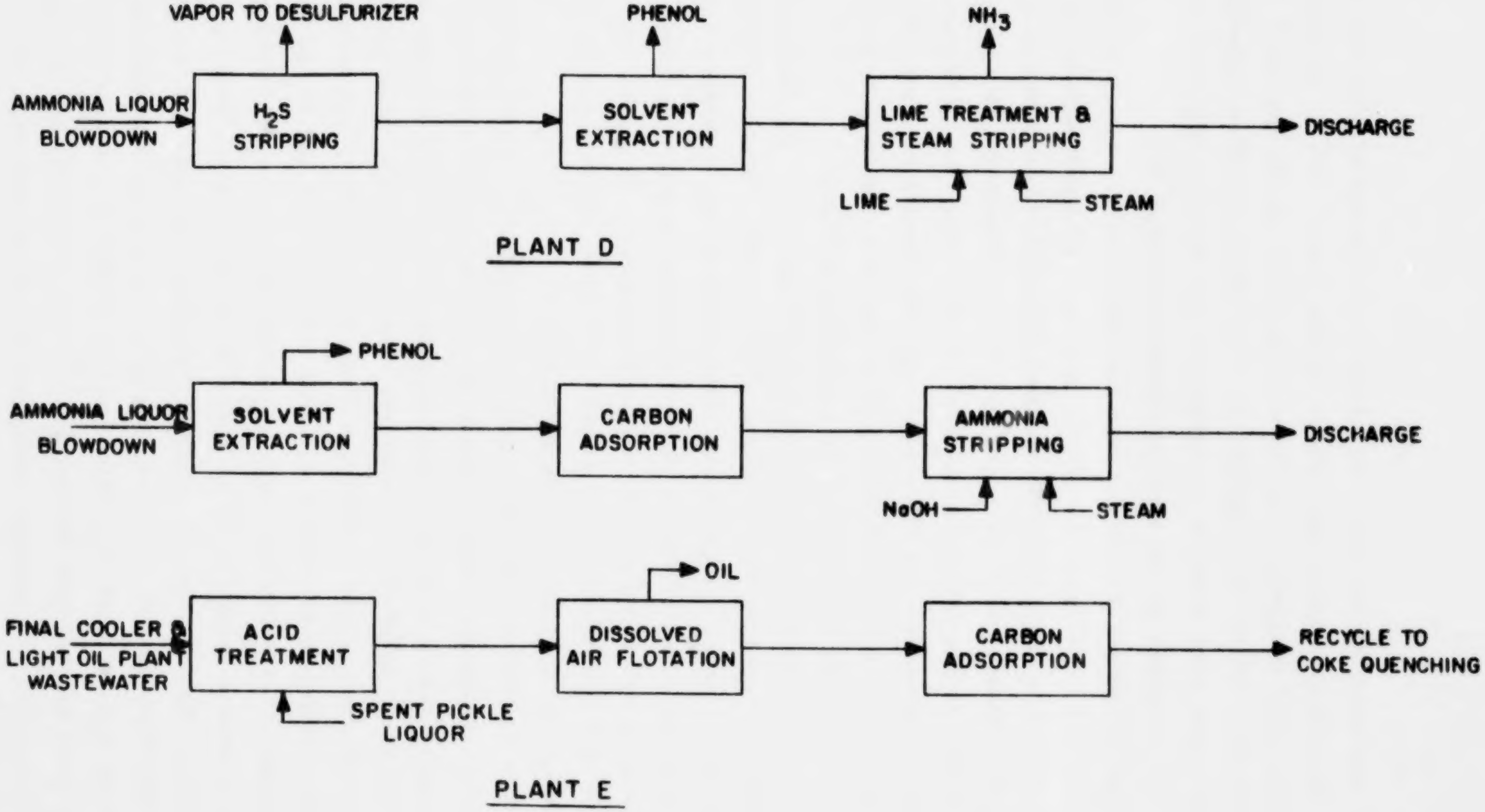

VAPOR TO DESULFURIZER
PHENOL
NH_3
AMMONIA LIQUOR
BLOWDOWN
H_2S STRIPPING
SOLVENT EXTRACTION
LIME TREATMENT & STEAM STRIPPING
DISCHARGE
LIME
STEAM
PLANT D
PHENOL
AMMONIA LIQUOR
BLOWDOWN
SOLVENT EXTRACTION
CARBON ADSORPTION
AMMONIA STRIPPING
DISCHARGE
NaOH
STEAM
OIL
FINAL COOLER &
LIGHT OIL PLANT
WASTEWATER
ACID TREATMENT
DISSOLVED AIR FLOTATION
CARBON ADSORPTION
RECYCLE TO
COKE QUENCHING
SPENT PICKLE
LIQUOR
PLANT E

Figure 7-5 (Pg. 2 of 2). Coke plant wastewater treatment systems.

Before discharge to the receiving stream, the treated process wastewater is mixed with once-through, non-contact cooling water. The quantities of the treated process wastewater and the cooling water are 60 gpm and 5,220 gpm, respectively. (Note: Bibliography 21, from which the above information was obtained, gave data based on the composite effluent stream. The data shown in Table 7-8 are based on the ammonia liquor wastewater only.)

Plant E--Phenol is removed from the waste ammonia liquor by solvent extraction (which reduces the phenol loading from 1,600 mg/l to 30 mg/l) followed by an activated carbon system. Ammonia is next removed by steam stripping. Final cooler and light oil plant wastewaters are treated with spent pickle liquor (and caustic soda, if necessary, for pH adjustment) followed by dissolved air flotation. The wastewaters are next treated in an activated carbon system before recycling for coke quenching. Both the carbon absorption systems are preceded by a multimedia filter.

Table 7-8 gives the wastewater characteristics of the feed going to the different treatment plants described above. Table 7-9 gives the overall removal efficiency of the different pollutants by the treatment schemes.

Steam stripping of wastewater specifically to remove hydrogen sulfide is not generally practiced in the coke oven industry. In Figure 7-5, Plant D is shown to have a H_2S stripper. However, no removal efficiency or design information was available in the literature.

Other variations and new control technologies are being applied in wastewater treatment. Some of these developments are discussed below.

Ammonia can be removed economically by the Phosam-W Process, details of which are given later in this section. Ion exchange has been tried for ammonia removal but the cost is excessive. A new development in recovery of coke oven byproducts from ammonia liquor blowdown and coke oven gas is the pairing of two systems: the Firma Carl Still desulfurization process (discussed earlier) and the Phosam-W process. Armco Steel Co. at Middletown, Ohio is constructing this plant. This system will recover anhydrous ammonia from the ammonia liquor blowdown and the coke oven raw gas, and recover a concentrated sour gas containing H_2S, HCN and CO_2, which will be burned in a sulfuric acid plant to produce acid gas and also destroy HCN(18). A commercial wet air oxidation system, designed to eliminate thiocyanates and cyanides from coke oven waste liquors, is being purchased by DOFASCO from Zimpro, Inc. The expected removal efficiency of the system is 99.9 percent for cyanides.

TABLE 7-8. CHARACTERISTICS OF BYPRODUCT COKE PLANT AMMONIA LIQUOR WASTEWATER(21)

	Plant Identification				
	A	B	C	D	E
Flow, gal/ton	139	127	41	46	N/A
Flow, gpm	490	390	169	53	150
Ammonia, mg/l	1,900	1,380	7,330	3,900	5,000
BOD_5, mg/l	1,500	1,280	1,120	1,200	N/A
Cyanide, mg/l	102	110	91	N/A	20
Oil & grease, mg/l	N/A	240	101	210	1,000
Phenol, mg/l	450	350	910	610	1,600
Sulfide, mg/l	N/A	629	197	420	N/A
Suspended solids, mg/l	N/A	36	421	2,300	N/A

TABLE 7-9. CONTAMINANT REMOVAL EFFICIENCY OF BYPRODUCT COKE OVEN PLANT TREATMENT FACILITIES(21)

	% Overall Removal Efficiency				
	A	B	C	D	E
Ammonia	44.6	28.8	92.9	95.3	99.0
BOD_5	95.4	98.5	47.7	61.2	N/A
Cyanide	89.6	71.8	18.4	N/A	N/A
Phenol	99.6	99.8	73.4	99.1	99.9
Oil & grease	N/A	99.1	80.2	99.5	99.5
Suspended solids	N/A	N/A	74.4	76.6	N/A
Sulfide	N/A	99.96	37.0	64.4	N/A

Following are the major coke oven wastewater treatment processes, all of which are applicable to coal conversion waste treatment:

1. Ammonia removal and recovery processes (steam stripping followed by sulfuric acid treatment to form ammonium sulfate, or Phosam-W process producing anhydrous ammonia);
2. Biological oxidation;
3. Activated carbon adsorption;
4. Oil removal processes (API gravity separators and dissolved air flotation); and
5. Phenol removal processes (solvent extraction, biological oxidation and activated carbon adsorption).

Details of these processes and their operating experiences from coke oven applications are given below:

Ammonia Removal and Recovery

Ammonia removal and recovery from the coke oven wastewaters is very common as already shown in Figure 7-5. Steam stripping of ammonia from the wastewater and absorption of the resulting ammonia vapor in the coke oven gas saturator with sulfuric acid to yield ammonium sulfate as a byproduct is the most common treatment. An alternate ammonia recovery process is the Phosam-W, whereby an anhydrous ammonia byproduct is recovered from the wastewater. A few plants strip ammonia from the wastewater and incinerate the resulting vapors.

Ammonia Stripping--

The ammonia concentration of the flushing liquor (ammonia liquor blowdown) varies between 3,000 to 9,000 mg/l, a concentration range generally found for the coal conversion process wastes also. At least half of the ammonia in the above coke oven wastewater is in the fixed form, mostly as ammonium chlorides and some as ammonium sulfides, cyanide and thiocyanate, etc. When the ammonia liquor blowdown is steam stripped without pH adjustment, only the free ammonia will be removed as is the case of the "free leg" stripping process. For greater ammonia removal, the fixed ammonium is liberated by treating with an alkali before steam stripping. Most of the plants use lime for pH adjustment and freeing ammonia. A pH of at least 11.0 is required to liberate all fixed ammonia. Lime consumption is substantial, being in the order of 1.0 pounds per ten gallons of wastewater.

Caustic can be used in place of lime for pH adjustment with attendant higher operating cost. Plant E in Figure 7-5 was found to use caustic and claimed the following advantages:

- Stripping steam requirements were reduced by about 50 percent over a lime still at the same ammonia removal efficiency,
- Accurate pH control was obtained, and
- The disadvantage of a lime sludge disposal problem was eliminated.

Lime treatment followed by steam stripping, however, is the principal control technology for ammonia in the coke oven industry.

The ammonia stripping tower consists of a distillation column containing mostly stripping trays, one or two rectifying trays and a partial condenser (also called dephlegmator). The overhead vapor product generally contains about 25 percent ammonia, which is sent to an existing coke oven saturator where an ammonium sulfate byproduct is produced. The tower bottoms contain around 50 to 100 mg/l of ammonia when the pH of the feed to the tower is maintained around 11.0 and adequate steam is used for stripping. The steam requirement is between 0.1 to 0.2 lb per pound of feed to the tower.

Several types of distillation columns are in use. The older plants use bubble cap distillation columns, each containing a "free leg" section and a "fixed leg" section. The liquid entering the fixed leg section is treated with lime to free the fixed ammonia. Newer plants use various modifications of the above column or completely new types of distillation trays.

Applications--

Steam stripping will be used to remove hydrogen sulfide and ammonia from coal conversion wastewaters whenever the levels of H_2S and NH_3 are high (approximately 1,000 ppm or greater). Steam stripping with ammonium sulfate recovery has been used in a commercial coal conversion complex in Sasol, South Africa. All of the commercial coal gasification and liquefaction processes under design consideration in the U.S. show steam stripping of sour process wastewaters for ammonia and hydrogen sulfide removal.

Phosam-W Ammonia Removal and Recovery--

The U.S. Steel Phosam-W process has been in use in a dozen or more installations around the world to recover ammonia from coke oven plants. The process has been used to recover ammonia from both the coke oven gas and the ammonia liquor wastewater stream. To recover ammonia from coke oven gas a scrubber (an absorber) is used to remove ammonia and form an ammonium phosphate solution, which is then steam stripped to regenerate it for re-use. The stripper overhead vapor is next fractionated in a distillation column to yield anhydrous ammonium product.

To remove and recover ammonia from the ammonia liquor blowdown, the wastewater is first steam stripped in a sour water stripper (see Figure 7-6). The rest of the system remains the same. The stripper overhead vapor is sent to a scrubber where ammonium phosphate solution is used to absorb ammonia. The rich solution is thermally regenerated to yield fresh solution for recycle to the absorber and a vapor containing ammonia and steam. The vapor stream is next fractionated to yield anhydrous (99.9% pure) ammonia.

The treated wastewater from the Phosam-W process will contain about 50 ppm of ammonia provided the fixed ammonia in the wastewater feed is liberated by pH adjustment to around 11.0.

The difference between the Phosam-W and the conventional steam stripping followed by sulfuric acid absorption is that the former produces anhydrous ammonia and the latter ammonium sulfate as the recovered byproduct. Byproduct utilization and market conditions will dictate which of the two processes is the preferred one for a particular situation. Anhydrous ammonia product has the advantage of easy marketability and higher product value. Primarily for this reason, the Phosam-W process has been recommended for application to coal conversion wastewaters in two recent studies(13)(30).

Biological Oxidation

Oxidation of dissolved and colloidal organic matter in wastewater by bacteria and other microoganisms to carbon dioxide and settleable organic sludge (consisting primarily of dead and live microorganisms) is a net result of biological oxidation systems. Various biological treatment systems have been tested in the pilot plant scale level with the coke oven ammonia liquor wastewater, e.g., activated sludge, aerated lagoon, trickling filter and rotating biological contactor. The activated sludge process has given the best results, and full scale treatment plants in the coke oven industry are generally of this type.

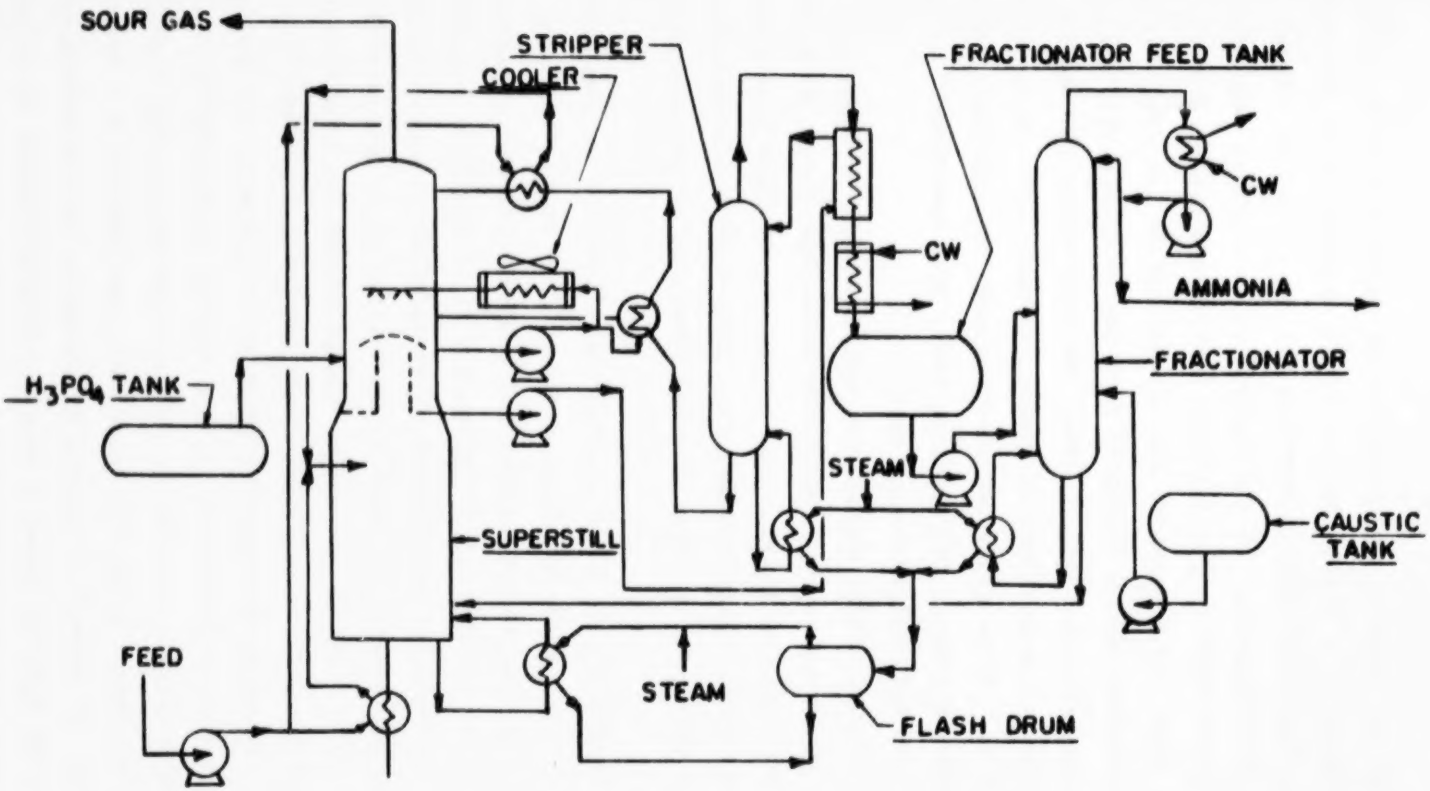

SOUR GAS
STRIPPER
COOLER
FRACTIONATOR FEED TANK
CW
CW
AMMONIA
FRACTIONATOR
H_3PO_4 TANK
STEAM
SUPERSTILL
CAUSTIC TANK
FEED
STEAM
FLASH DRUM

Figure 7-6. Phosam-W ammonia recovery process.

In the activated sludge process, new wastewater after being equalized (and neutralized, if necessary) is fed to an aeration or reaction tank where sufficient detention time is provided for the oxidation removal of the dissolved and colloidal organics. If the wastewater is nutrient deficient, nitrogen and phosphorus are added to the reaction tank in a minimum ratio of 100:5:1 of BOD:N:P. Also, the wastewater feed is admixed in the reaction tank with active, microbial solids collected from the secondary settling (clarifier) tank that follows the reaction tank. By controlling the recycle rate and concentration, a proper food to biological mass ratio in the reaction tank can be maintained. In an activated sludge system the important design parameters are: detention time in the reaction tank, MLSS concentration, clarifier overflow rate and sludge wasting rate.

An activated sludge system has been operating successfully with the ammonia liquor wastewater at Bethlehem Steel Coke Plant, Bethlehem, PA since 1962. Since then, other activated sludge systems have been constructed and operated with coke plant wastewaters. Table 7-10 shows the typical design parameters and operating data obtained from some actual activated sludge systems.

The Bethlehem coke plant studied the effects of various factors on phenol oxidation by the activated sludge process(37). Phenol loadings, ammonium ion concentrations, tar concentrations and temperatures were important variables. Although phenol loadings of 30 lb/day/100 cu ft could be successfully biooxidized, the system was difficult to operate due to excessive foaming. At phenol loading rates below about 12 lb/day/100 cu ft and at a phenol-to-sludge ratio 0.7 lb/lb MLSS, the activated sludge system has been operating well. Phenol removals of 99.8 to 99.9 percent are being achieved. BOD removal efficiency, however, has ranged from 85 to 95 percent. A portion of the wastewater organics, therefore, is not readily biodegradable.

The concentration of ammonia in the reaction tank has a significant effect on the phenol oxidation rate. Although ammonia is a nutrient source of nitrogen for the bacteria, ammonia in concentrations exceeding the range of 1,800 to 2,000 mg/l has shown a severe inhibitory effect on microbial growth. Since the coal conversion wastewaters, including the coke oven ammonia liquor, contain much higher levels of ammonia than the above range, ammonia removal pretreatment will have to be incorporated before the biological system.

TABLE 7-10. DESIGN AND OPERATING CONDITIONS OF SOME COKE PLANT ACTIVATED SLUDGE SYSTEMS

	(1)	(2)	(3)	(4)
Wastewater Parameters				
Influent phenol, mg/l	1,400	250 - 475	260 - 400	3,000
Effluent phenol, mg/l	0.1	0.1 - 0.3	0.8 - 3.6	0.1
BOD removal, %	85 - 95	N/A	N/A	N/A
Operating Conditions				
NH_3 concentration in aeration tank, mg/l	2,000	N/A	<1,200	N/A
pH	6 - 8	7 - 8	N/A	N/A
Temperature, °F	80 - 100	>70	N/A	N/A
F/M, lbs phenol per lb MLSS per day	0.7	0.2 - 0.25	N/A	N/A
MLSS, mg/l	3,300 - 4,700	2,500 - 3,500	N/A	2,500 - 3,000
Aeration time, hrs	56	24	37	114

(1) Data from Bibliography 37.
(2) Data from Bibliography 9.
(3) Data from Bibliography 9.
(4) Data from Bibliography 37.

Dissolved tars present in the hot ammonia liquor adversely affect phenol removal by bio-oxidation. This is probably due to occlusion of the microbial cells by precipitated tars. Storing ammonia liquor at ambient temperature to decrease the solubility of the tars or lime treatment of the hot liquor followed by clarification prior to biological treatment was found to be a satisfactory control technology that solved the problem.

Temperature at the biological reaction tank has a significant effect on phenol oxidation. The optimum temperature is around 95°F. Adequate phenol removal efficiency is obtained at a temperature range between 70 to 100°F range: 99.8 percent in the temperature range of 80 to 95°F and 99.6 percent at 70°F or 100°F.

The Bethlehem Steel Coke Plant wastewater, which has a pH range of 8.3 to 8.8, is directly fed to the activated sludge system without pH adjustment. Dilution of the wastewater is done, however, with cooling water in order to reduce the ammonia and dissolved solids concentrations at the biological reaction tank.

Foaming in the aeration tank is an operating problem. It is controlled by antifoam agents along with water sprays. The reasons for foaming are not fully understood. Coal mixes, coking practices and phenol loadings have effects. Increased phenol loadings increase foaming.

Thiocyanates and cyanides generally cause problems in a biological treatment process. However, although they are present in the coke oven ammonia liquor, the activated sludge process has performed smoothly. This is probably because of acclimation enhanced by the presence of phenol. In fact, the Bethlehem system has been able to degrade about 70 percent of the thiocyanates by oxidation. Cyanide oxidation efficiencies, however, have been erratic. During periods of good thiocyanate oxidation, cyanide reduction through (equalization) storage and bio-oxidation was around 70 percent. Other times, efficiencies have been poor. For consistent cyanide removal to a low level, alkaline chlorination of the bio-effluent would be necessary.

Since coal conversion wastewaters are similar to coke oven ammonia liquors, biological oxidation systems should be applicable to this treatment for the removal of phenols and other dissolved organics. Coal conversion wastewaters, especially from low-temperature gasification and liquefaction processes, will contain various types of phenolics, some of which have low biodegradability.

The activated sludge process applied to these waste streams will probably require additional detention time and more severe treatment than the coke oven wastewaters. The pilot scale bio-test works at the Wilsonville and the Fort Lewis, Washington, facilities showed this to be true. The waste treatment experience at the above two facilities and the trickling filter plant operation experience at the Sasol Plant complex indicate that biological treatment of the coal conversion wastewater is practical. Prior removal of ammonia, sulfide, and phenolics are, however, suggested pretreatment requirements. Actual pilot tests with real waste streams from the particular coal conversion system will be necessary to arrive at optimum design conditions and to ensure reliable treatment plant operation.

Carbon Adsorption

Activated carbon treatment of coke plant wastewaters has been successful in removing phenol, color, COD and BOD in both pilot plant and full scale wastewater treatment systems. The first full-scale system went on stream in 1976 at the Cleveland District Coke Plant, a Republic Steel Corporation facility. Figure 7-5, Plant E, shows the block flow diagram of the above treatment facility. The ammonia liquor blowdown, containing about 1,600 mg/l of phenol, is first dephenolized to a level of 30 mg/l by solvent extraction before carbon adsorption is utilized. Other low strength wastewaters containing around 40 mg/l of phenol are treated with activated carbon after oil and suspended solids removal.

Phenol concentration in the effluent can be reduced to as low as 0.01 mg/l by carbon adsorption. The above plant, however, is operated to meet around 1 mg/l phenol level. Excellent color removal is attained, which is not the case with biological treatment of the coke plant wastewater. Negligible cyanide and ammonia removal are obtained, however, from carbon treatment.

Carbon usage at the Cleveland District Coke Plant is about 5.3 pounds per 1,000 gallons of wastewater. Other design conditions were not given(44). However, in a pilot study to determine the design conditions of a carbon adsorption system for the coke plant wastewaters, it was determined that wastewater contact time of about 60 minutes was necessary; and the wave front length was about 5 ft at the test conditions(50).

Advantages of carbon adsorption are many. It is a physical process which is not affected by toxic pollutants; and it can handle fluctuations in waste loads. Influent wastewater varying from 2 to 30°C did not show much effect on removal efficiency. However, carbon is expensive. Regeneration requires a lot of energy. At the Cleveland District Plant, it is felt that the physical-chemical treatment (Plant E in Figure 7-5) of the coke plant wastewater is competitive with the physical-biological treatment systems.

Carbon adsorption probably will have applicability in coal conversion wastewater treatment, especially for final polishing treatment and pretreatment of wastestreams that contain toxic and refractory substances. Due to the differences in the characteristics of the coal conversion and coke oven wastewaters, the performance and design conditions might be different. Laboratory tests with actual coal conversion wastewater will be necessary (adsorption isotherm and column runs) before full-scale plant design.

Some coal conversion systems generate char as a byproduct, which is utilized in a gasifier, e.g. COED process. If it could be possible to utilize the byproduct char as an activated carbon, then carbon treatment of the wastewater for that system will become very economical, since regeneration will not be necessary. The spent carbon would be combusted/gasified in the usual manner. Whether or not char will behave as an activated carbon is to be determined on a case-by-case basis. The coke or fine coals generated in the coke oven process, however, has not been successfully used to remove phenol and dissolved organics from the coke oven wastewaters(50).

Oil Removal

In the coke oven wastewater treatment both API separators and dissolved air flotation (DAF) systems are used to remove oils. API separators are used to remove oils from storm water runoffs and from process wastewaters generated in the light oil recovery and refining section of the Byproduct coke oven plant. Dissolved air flotation is used to remove emulsified oils (an example is shown in Figure 7-5, Plant E).

API gravity separators and DAF systems will be the primary treatment of oily wastewaters in coal conversion plants. Such wastewaters include process wastewaters and storm water runoffs from the coal conversion complex. All developing coal conversion plants in the U.S. use these types of treatment for oily-waste waters. The wastewater treatment systems at the South African and Yugoslavian Lurgi plant complexes also use them.

Phenol Removal and Recovery

Phenols are being removed from coke oven weak ammonia liquor by solvent extraction, steam stripping and/or biological oxidation. Steam stripping for phenol removal is not a common treatment application. Phenol forms a minimum boiling point azeotrope with water at 9.2 percent (by wt.) phenol, and therefore, stripping requires large amounts of steam, and proves to be uneconomical. Biological oxidation removal efficiencies of phenol, as discussed earlier, are high (99.8 to 99.9%), but requires proper plant design and operation. Fluctuations in influent phenol composition can create upset conditions in the biological system. Solvent extraction, however, can more reliably handle feed fluctuations and recover byproduct phenol from the waste stream. Solvent extraction becomes most economical with highly contaminated streams and with biological oxidation for dilute streams. Solvent extraction becomes competitive with biological oxidation at phenol concentrations of about 1,000 mg/l (waste flow rates above 50 gpm).

The earliest large-scale use of solvent extraction for phenol recovery from coke oven wastewater was done in Germany. Benzene or light oil solvent was used in some processes to extract phenolics. Regeneration of the benzene (or light oil) was accomplished with caustic extraction. The process thus recovered phenolics as sodium phenolate. Another process used tricresyl phosphate as a solvent for phenol extraction. Both these processes are discussed in detail in the following sections.

Newer proprietary processes are presently available for phenol extraction which claim to be more economical. These processes use volatile solvents which are easier to recover during regeneration steps. The Phenosolvan process is one which has been used commercially to recover phenol from Lurgi process gas liquor in South Africa and Yugoslavia (see Figure 5-2). This process uses isopropyl ether as the solvent. Details of the Phenosolvan process are discussed elsewhere(30), and therefore, will not be covered here. The Phenosolvan process is likely to be used in several of the presently planned coal gasification projects in the U.S.

Jones and Laughlin Steel Corp. has developed a proprietary solvent extraction process which has been used in several coke plants in the U.S. The process can recover 99+ percent pure phenol and generate an effluent containing about 1 ppm of phenol. It uses a Karr reciprocating plate extractor for phenol extraction (the type of solvent used is proprietary information), a solvent stripper and a distillation column to produce pure phenol.

To illustrate the types of equipment involved in solvent extraction the light oil (benzene) - caustic process and the tricresyl phosphate process, the two earliest processes still in use, are discussed in detail in the following sections.

Light Oil - Caustic Process--

The phenolized ammonia liquor is pumped into the distributor header located near the top of the ammonia liquor scrubber (see Figure 7-7). The liquor passes downward through the scrubber and comes in contact with a counter-current flow of light oil. The light oil, having a lower specific gravity than the liquor, rises to the top of the column as it extracts the phenol from the liquor. The ammonia liquor falls to the base of the column and is pumped away for further treatment.

The phenolized light oil flows out the top of the ammonia liquor scrubber to the caustic washer in the caustic treatment tower.

The caustic treatment tower is divided into three compartments. The bottom chamber is the light oil circulation tank which is the pumping chamber for the dephenolized light oil. The upper two sections are the caustic washing compartments, packed with ceramic tile. In these compartments, the phenolized light oil passes through the caustic to remove the phenols by chemical reaction between the caustic and the phenols, as follows:

$$\underset{\text{phenol}}{C_6H_5OH} + \underset{\text{sodium hydroxide}}{NaOH} \longrightarrow \underset{\text{sodium phenolate}}{C_6H_5ONa} + \underset{\text{water}}{H_2O}$$

The phenolized light oil passes from the ammonia liquor scrubber to the distributor header on the No. 1 washer to a distributor header on the No. 2 washer to the overflow line, where the light oil, now dephenolized, is returned to the circulation tank.

After about a week, the caustic in the No. 1 washer is saturated with phenols. At this point, the recovery operation is shut down so that the spent caustic can be replaced by fresh solution.

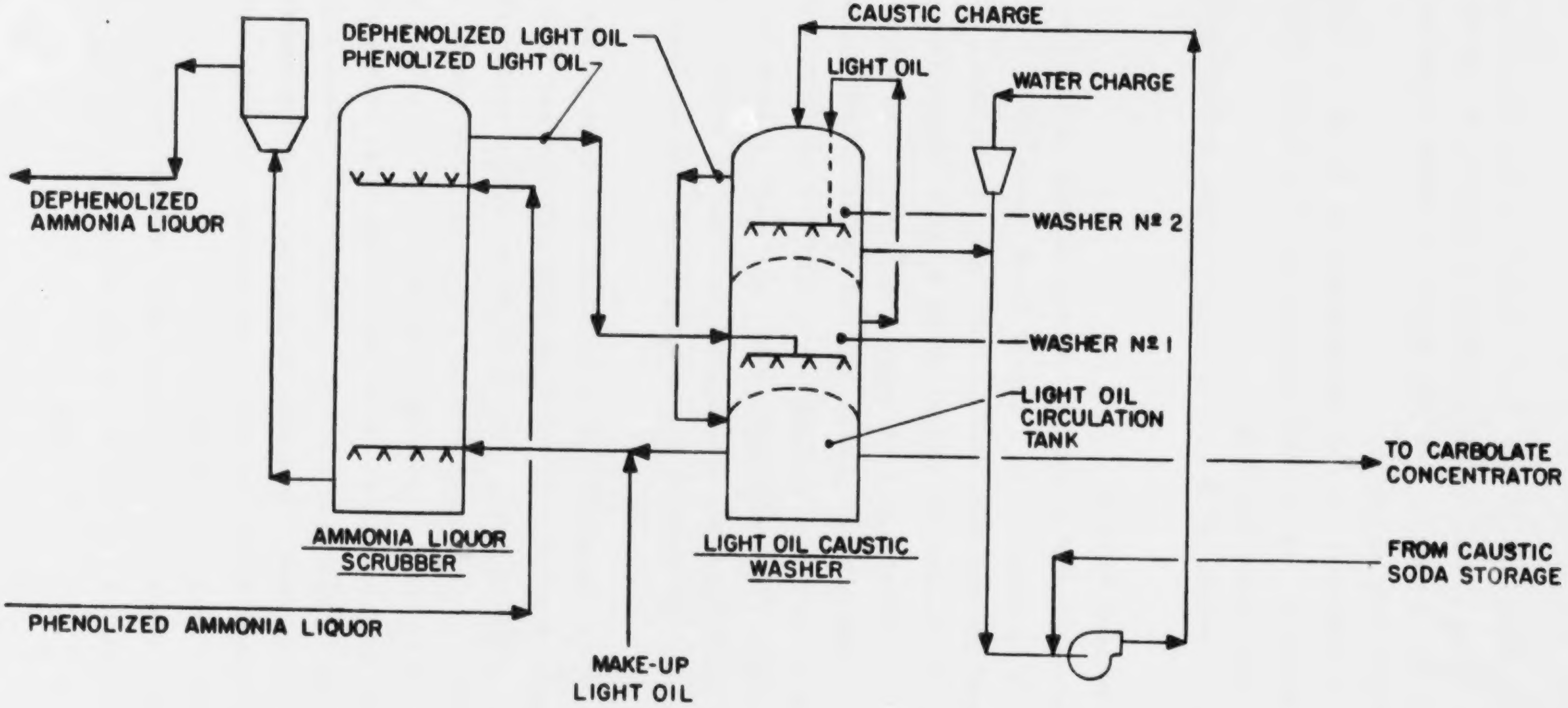

DEPHENOLIZED LIGHT OIL
PHENOLIZED LIGHT OIL
CAUSTIC CHARGE
LIGHT OIL
WATER CHARGE
DEPHENOLIZED AMMONIA LIQUOR
WASHER Nº 2
WASHER Nº 1
LIGHT OIL CIRCULATION TANK
TO CARBOLATE CONCENTRATOR
AMMONIA LIQUOR SCRUBBER
LIGHT OIL CAUSTIC WASHER
FROM CAUSTIC SODA STORAGE
PHENOLIZED AMMONIA LIQUOR
MAKE-UP LIGHT OIL

Figure 7-7. Phenol removal by light oil -- caustic process.

The sodium phenolate in the No. 1 washer is drained into the carbolate concentrator. Then the partially phenolized caustic in the No. 2 washer is drained to the No. 1 washer, leaving the No. 2 washer empty to receive a fresh supply of caustic soda solution.

The sodium phenolate in the concentrator is boiled to remove entrained solvent and moisture. It is then neutralized with carbon dioxide to liberate crude phenols and phenol homologs.

The phenol removal efficiency of this process can be expected to be at 98 to 99 percent.

High-Boiling Solvent Process--

Extraction with a high-boiling solvent allows for direct phenol recovery by distillation or possibly by a simple flash operation. A solvent such as tricresyl phosphate has been used in this type of process. This solvent has a distribution coefficient for phenol about 8 times larger than that for benzene, and is virtually immiscible with water (solubility < 15 ppm). Distillation can be used to separate the phenolics from the tricresyl phosphate, and since the latter has a very high boiling point (265°C @ 10 mm Hg), vacuum distillation should be a simple flash operation where the spent solvent is heated in a series of interchangers and exchangers, and flashed across a control valve into a tank where the phenols are vaporized and removed from the solvent (see Figure 7-8).

The result of the distillation or flash operation is the recovery of a very pure phenol product. One problem with this process is that less volatile phenolics and other organics tend to build up in the recirculated solvent, causing problems of increased viscosity and decreased phenol capacity. Two solutions are possible: either the process can be shut down and loaded with fresh solvent, when necessary, or a continuous purge stream can be removed from the system to maintain a steady concentrate of heavier phenolics and organics in the solvent. Disposal of the spent solvent becomes a problem. When these disposal costs are taken into account, this process becomes less attractive for a large size plant.

The phenol removal efficiency of this process can be expected to be at 95 to 99 percent, depending upon the design of the system.

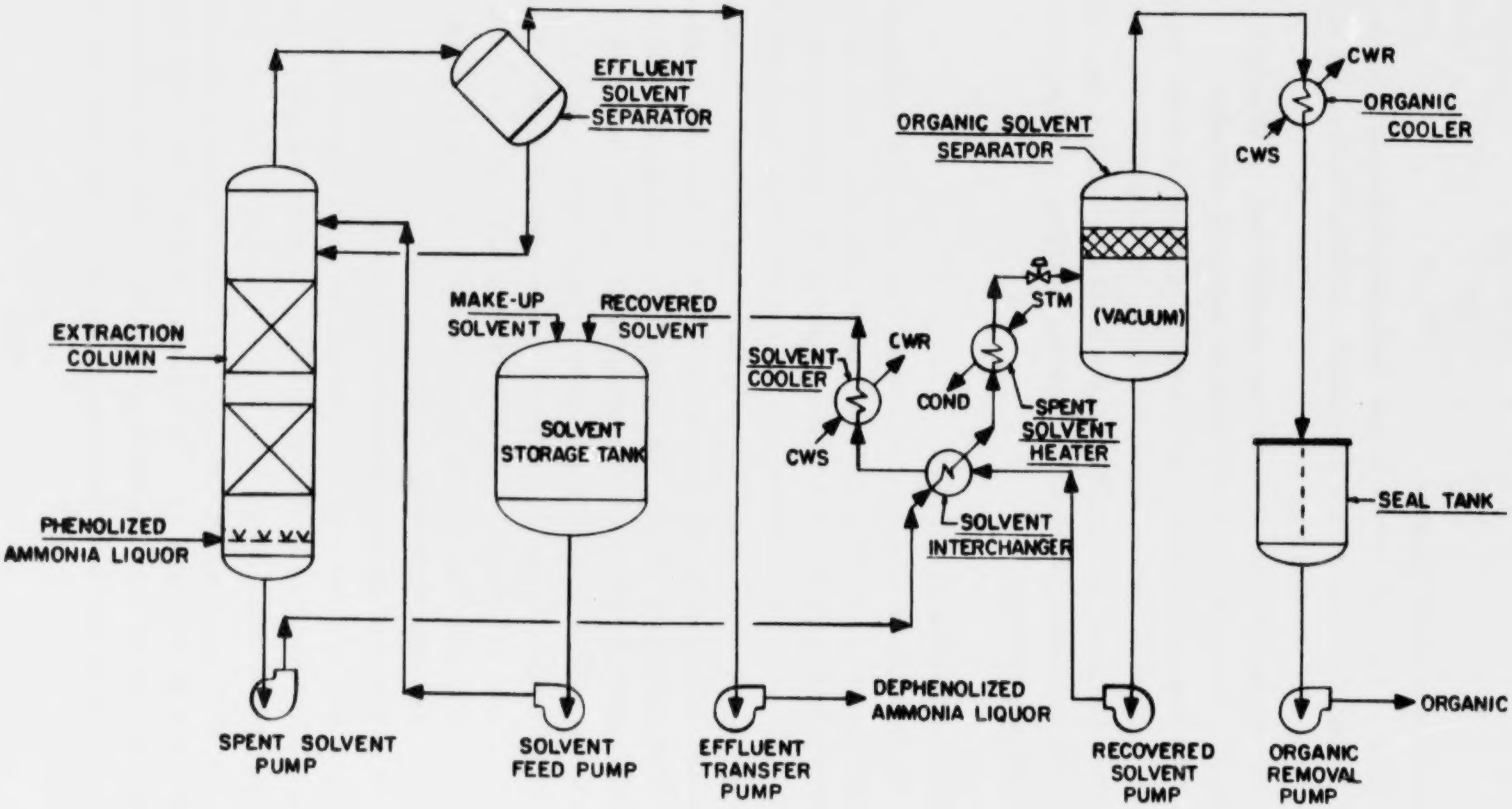

EFFLUENT SOLVENT SEPARATOR
ORGANIC SOLVENT SEPARATOR
CWR
ORGANIC COOLER
CWS
EXTRACTION COLUMN
MAKE-UP SOLVENT
RECOVERED SOLVENT
SOLVENT STORAGE TANK
SOLVENT COOLER
CWR
CWS
STM
COND
(VACUUM)
SPENT SOLVENT HEATER
SOLVENT INTERCHANGER
SEAL TANK
PHENOLIZED AMMONIA LIQUOR
DEPHENOLIZED AMMONIA LIQUOR
ORGANIC
SPENT SOLVENT PUMP
SOLVENT FEED PUMP
EFFLUENT TRANSFER PUMP
RECOVERED SOLVENT PUMP
ORGANIC REMOVAL PUMP

Figure 7-8. Phenol removal by high boiling solvent process.

SOLID WASTE DISPOSAL METHODS

Most of the sump breeze (coke) collected from quench water circuits is sold (primarily, larger size fractions), recycled to the coal pile, or used in the sinter mix in steel mills.

Tar sludge obtained from the tar storage tank is usually disposed of by landfill. Incineration is an alternate method of disposal.

Coke oven plants utilizing biological systems to treat wastewater generate an excess biomass residue which is usually landfilled.

The coke oven gas desulfurization processes convert the sulfur in the off-gases to commercial elemental sulfur, sulfate, or sulfuric acid, instead of producing residues.

LIGHT OIL UPGRADING PROCESSES

Light oils and coal tars are two of the coke oven byproducts which are further refined to produce upgraded usable products. Coal tar processing is generally done outside the coke oven industry by chemical companies, and therefore, will not be covered in this report, since it is beyond the scope of this study. However, light oil refining is extensively done by the coke oven industry; consequently, it will be discussed in subsequent paragraphs.

Coke oven light oil is rich in benzene, toluene, and xylene (BTX). However, these aromatics are contaminated by various compounds such as paraffins, naphthenes, olefins and sulfur pollutants (see Table 7-11 for a typical light oil composition). These contaminants can be reduced by the following processes:

1. Acid treatment followed by caustic soda wash and distillation;
2. Hydrogenation followed by extraction and distillation; and
3. Hydrodealklation by the LITOL process.

Acid treatment is the traditional method for purifying light oil. The yields of BTX products from this process are lower and the sulfur content of benzene produced by acid washing is higher (100 to 400 ppm of thiophene) compared to the Litol process.

The multiple steps in the extraction process will produce high quality aromatics from the light oil. It appears, however, that the capital and operating costs of this process will be higher than the LITOL process. No commercial plant has been built to upgrade coke oven light oil using this process.

TABLE 7-11. TYPICAL RAW LIGHT OIL COMPOSITION

Component	Wt %
Cyclopentadiene	0.35
C_5-C_6 Non-aromatics	0.06
Benzene	73.46
Thiophene	0.44
C_7-C_8 Non-aromatics	0.02
Toluene	14.82
Xylenes & Ethylbenzene	3.03
Styrene	1.55
Carbon Disulfide	0.45
Propylbenzene	0.05
Mesitylene	0.14
Pseudocumene	0.25
Dicyclopentadiene	0.33
Diethylbenzene	0.05
Coumarone	0.31
Indene & Durene	1.98
Naphthalene	1.83
Dimethylnaphthalene	0.43
Other Methylnaphthalenes and Higher Homologs of Benzene	0.45
	100.00

The LITOL process, which was developed by the Houdry Division of Air Products and Chemicals, Inc., has been employed commercially since 1964 to produce high quality (even reagent grade) benzene from coke oven light oils. Seven commercial plants have been build worldwide utilizing the LITOL process. It is anticipated that LITOL will be applied widely for upgrading coal gasification and liquefaction derived light oils (naphthas) in the future.

LITOL Process

The Houdry LITOL process is a catalytic process with two principal reaction zones: a hydrogenation section, and a hydrocracking/dealkylation/desulfurization section. Various chemical reactions occur within the LITOL reactors. Figure 7-9 shows some of the major ones. Hydrodealkylation reactions dominate, explaining why the Litol process produces mostly high-quality benzene with very little C_8 aromatics.

Figure 7-10 depicts the flow diagram for the LITOL process. The crude light oil is pumped to unit pressure (700 to 900 psig), heated to 1,050 to 1,150°F, and vaporized by contact with a hot hydrogen stream. The vaporized charge is taken overhead while a small amount of tar (styrene polymer) is withdrawn as bottoms product. The overhead vapors flow through a pretreat reactor for saturation of the remaining styrenes and through a fired heater to bring the light oil hydrogen stream up to reaction temperature. The preheated feed flows through the reactors (which contain a chromia-alumina catalyst), exchanges heat with the feed streams, and is flashed in a high-pressure flash drum.

The non-aromatic materials - mainly paraffins, olefins, diolefins, naphthenes, and sulfur compounds - are completely converted to lighter hydrocarbons and to hydrogen sulfide. Substitute aromatics are partially hydrodealkylated to produce additional benzene.

The vapors from the flash drum (after the reactors) divide, a portion being vented to fuel while the rest are recycled to generate hydrogen. The flashed liquid flows to a stabilizer tower for removal of light ends, through a clay treater for removal of trace olefins and then to product fractionation.

HYDROCRACKING

1. $$\underset{\text{2, 4 - Dimethyl Pentane}}{CH_3\text{-}CH(CH_3)\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_3} + H_2 \longrightarrow \underset{\text{Propane}}{C_3H_8} + \underset{\text{Butane}}{C_4H_{10}}$$

2. $$\underset{\text{Cyclohexane}}{C_6H_{12}} + 3H_2 \longrightarrow \underset{\text{Ethane}}{3C_2H_6}$$

3. $$\underset{\text{Cyclohexane}}{C_6H_{12}} + 2H_2 \longrightarrow \underset{\text{Propane}}{2C_3H_8}$$

HYDRODEALKYLATION

1. $$\underset{\text{Toluene}}{C_7H_8} + H_2 \longrightarrow \underset{\text{Methane}}{CH_4} + \underset{\text{Benzene}}{C_6H_6}$$

2. $$\underset{\text{Ethylbenzene}}{C_8H_{10}} + H_2 \longrightarrow \underset{\text{Ethane}}{C_2H_6} + \underset{\text{Benzene}}{C_6H_6}$$

HYDRODESULFURIZATION

1. $$\underset{\text{Thiophene}}{C_4H_4S} + 4H_2 \rightleftharpoons \underset{\text{Butane}}{C_4H_{10}} + H_2S$$

2. $$\underset{\text{Carbon Disulfide}}{CS_2} + 4H_2 \longrightarrow \underset{\text{Methane}}{CH_4} + H_2S$$

HYDROGENATION

1. $$\underset{\text{Styrene}}{C_8H_8} + H_2 \longrightarrow \underset{\text{Ethylbenzene}}{C_8H_{10}}$$

DEHYDROGENATION

1. $$\underset{\text{Cyclohexane}}{C_6H_{12}} \longrightarrow \underset{\text{Benzene}}{C_6H_6} + 3H_2$$

Figure 7-9. Typical LITOL reactions.

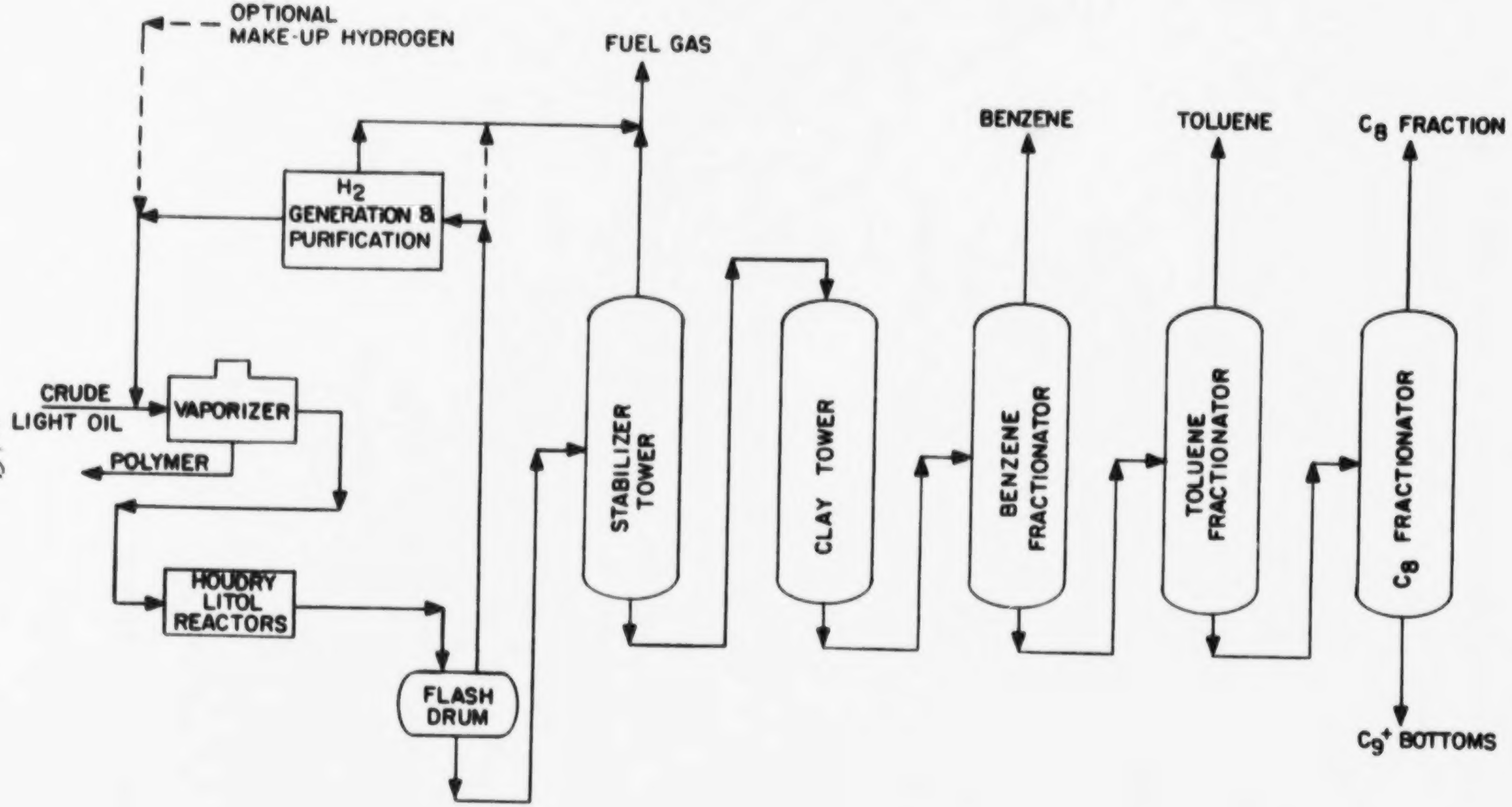

OPTIONAL
MAKE-UP HYDROGEN
FUEL GAS
H_2 GENERATION & PURIFICATION
CRUDE LIGHT OIL
VAPORIZER
POLYMER
HOUDRY LITOL REACTORS
FLASH DRUM
STABILIZER TOWER
CLAY TOWER
BENZENE
BENZENE FRACTIONATOR
TOLUENE
TOLUENE FRACTIONATOR
C_8 FRACTION
C_8 FRACTIONATOR
C_9^+ BOTTOMS

Figure 7-10. Houdry's LITOL light oil upgrading process.

Benzene product is separated from heavier aromatics by conventional distillation. The benzene tower bottoms, consisting primarily of toluene, can be recycled to the process for further conversion or can be further distilled to produce a toluene product with recycle of the bottoms from that tower. An additional tower can be used to separate C_8 aromatics from a heavier C_{9+} fraction.

The process is a consumer of hydrogen which can be generated readily in a steam methane reformer using the methane-rich recycle gas stream (flash drum vapor) as the feed stream. No outside source of gas is needed to maintain the required hydrogen balance. Hydrogen consumption is about 0.47 moles per mole of benzene product.

Typical yields from the LITOL process are shown in Table 7-12 for two cases: toluene recycle, and no toluene recycle. When higher benzene yield is desired, toluene can be recycled to the LITOL reactor for conversion to benzene by hydrodealkylation reaction (See Figure 7-7).

The installed capital cost of a LITOL facility to process 70,000 metric tons per year of coke oven light oil will be about $8.1 million dollars (1978 costs) approximately distributed as follows:

Unit	Installed Capital Cost
Feed Pretreatment	$ 800,000
Main LITOL	$4,800,000
Cryogenic	$1,300,000
Hydrogen Generation	$1,200,000
	$8,100,000

The operating costs of the plant are summarized in Table 7-13 which shows that the total cost per ton of benzene product is $153.34. Since the selling price of benzene is about $180.00 per metric ton, there is an economic incentive to refine the crude light oil. An additional benefit of the process is the removal of sulfur and nitrogen pollutants from the crude light oils which would contribute to our pollution problems, if not removed by upgrading. In the LITOL process, sulfur and nitrogen are converted to hydrogen sulfide and ammonia, which are subsequently removed by the purification steps associated with the hydrogen plant.

TABLE 7-12. TYPICAL LITOL PROCESS YIELDS

(Basis: 100 Ton of Raw Light Oil Feed)

	No Toluene Recycle		Toluene Recycle	
	Reactor Feed(1)	Products	Reactor Feed(1)	Products
Hydrogen	0.95	0.10	1.13	0.13
Hydrogen Sulfide		0.41		0.41
C_1-C_5 Hydrocarbons	0.53	6.80	0.59	8.13
C_6 Non-Aromatics	0.59	0.02	0.59	0.02
C_7 Non-Aromatics	0.21		0.21	
Benzene	74.09	86.66	74.09	92.88
Toluene	19.22	7.36	19.22	0.02
C_8 Non-Aromatics	0.09		0.09	
Xylene	3.12		3.12	
Ethylbenzene	0.22		0.22	
Styrene	0.62		0.62	
C_9+	0.70	0.01	0.70	0.01
Thiophene	1.02		1.02	
	101.36	101.36	101.60	101.60

(1) Includes makeup hydrogen (95 mol% H_2 and 5 mol% C_1 composition)

TABLE 7-13. LITOL PROCESS OPERATING COST

(Basis: 70,000 Metric Tons/yr of Light Oil Feed)

Item	Units	U.S. $/Metric ton of Benzene
Feedstock	$105/M.T.	142.27
Utilities		
Fuel	$8.00/MMKcal	11.27
Power	2.0¢/KWH	1.67
Steam	$7.00/M.T.	1.05
Cooling Water	0.8¢/M^3	0.31
Chemicals & Catalyst	-	0.55
Sub-total		157.12
Fixed Cost		
Operating Labor	$7.00/hr-4 men/shift	4.75
Operating Overhead	150% of Operating Labor	7.13
Maintenance	4% of Investment	6.27
Supplies (including N_2)	-	0.50
Insurance & Taxes	1% of Investment	1.57
Depreciation	15 years-Straight line	10.45
Sub-total		30.67
Credit		
Fuel Gas	$8.00/MMKcal	5.46
Fuel Oil	$75/M.T.	16.21
Toluene	$150/M.T.	12.78
Sub-total		34.45
TOTAL		153.34

NOTE: LITOL unit feed is 59,750 MTPY after prefractionation. Yields 51,650 MTPY of benzene and 4,400 MTPY of toluene.

The LITOL process is expected to have wide application in upgrading coal conversion system light oils. It has been considered for upgrading the light oils (naphthas) that will be produced from the proposed El Paso Lurgi process(55). Although the BTX concentrations of the naphtha from the referenced plant will be only 46.8 wt. percent as compared to about 85 percent for the coke oven light oil, upgrading of the naphtha is still considered to be economic.

The reason the BTX concentration in the naphtha from the El Paso Lurgi plant will be about 46.8 percent is that a sub-bituminous type coal will be used in the process. If, instead, a bituminous coal similar to the coal fed to the coke ovens, is used in the Lurgi process, the BTX concentrations in the Lurgi naphtha will also be about 85 percent. This dependence of BTX concentration on coal type in the light oil has been proven by the Lurgi gassification data.

At design conditions, 20,000 lbs/hr of naphtha byproduct will be produced from the El Paso Lurgi plant. Processing of this naphtha through the LITOL system will yield the following products:

	Quantities, lbs/hr
Benzene -	8,732
C_9+ -	1,000
C_5- -	1,000

The process will require 3,827 lbs/hr of make-up hydrogen. Waste streams from the above LITOL system will contain the following:

- A small stream of sour gas, 827 lbs/hr, which will contain about 5 percent H_2S and 4 percent NH_3.
- A small amount of process wastewater, 291 lbs/hr, which will require treatment for ammonia, sulfides and oil removal.

FUGITIVE EMISSIONS CONTROL

Air pollution control technology (existing and proposed) for the collection and removal of particulate matter and gaseous emissions in the Byproduct coke oven industry is discussed in subsequent sections. Since much of the air pollution control technology has been or is being developed around the coke oven batteries and coke quench systems, the major thrust of industry and manufacturers has been to focus on these areas of the plant for the control of the more obvious visible particulate matter, and gaseous emissions.

The coke ovens are a major source of air pollution emissions in the steel industry (15). Topside coke oven workers have a substantially higher risk of having cancer than the average worker (see Section 8 for details), probably from carcinogenic materials associated with the particulate fraction of the coke oven emissions. Various schemes to control the fugitive emissions and alleviate potentially adverse health effects are being developed. The Air Pollution Control Association and the EPA co-sponsored a conference on "Control of Air Emissions from Coke Plants" which was held in Pittsburgh, PA in April 1979. In this conference, various fugitive emission control technologies were discussed which are reflected below.

Coal charging emissions can be controlled by: staged charging with coke oven raw gas evacuation to the gas collecting main; larry cars with gas capturing equipment (e.g. hoods and ducts) and wet scrubbers; and pipeline charging (closed charging). Coking cycle emissions can be minimized by improved door sealing, but better control is obtained with sheds ducted to air pollution control devices (e.g scrubbers) whose main purpose is to control pushing (coke discharging) operation emissions. Other systems being developed for pushing emission control are various mobile and fixed duct collection systems integrated with control devices (e.g. scrubbers, fabric filters, electrostatic precipitators). Coke quenching emissions can be controlled by the use of a hooded quench system, or they can be significantly reduced by the use of dry quenching methods. A summary of the various coke oven control technologies for fugitive emissions are shown in Table 7-14. Many of these control methods will have applications in the synfuels industry in analogous situations.

Charging Emission Control

Coal is charged into the coking chamber through charging holes provided in the roof of the oven. The oven retort or coking chamber and the heating system are designed to process a coal charge of definite volume with a level upper surface approximately one foot below the oven roof. The coal is charged from a device called a larry car situated on tracks supported by the battery top. The charging of coal into coke ovens results in a fugitive emission consisting of coal dust, tars and gases from the changing hole. Several types of control technologies are available to contain emissions during oven charging.

TABLE 7-14. BYPRODUCT COKE OVEN FUGITIVE EMISSIONS CONTROL

Operation/Emission Source	Pollutants	Control Technology	Relative Control Efficiency*	Coal Conversion Applicability
Charging	Particulates, SO_x, hydrocarbons, CO, NO_x & ammonia	Staged/charging (with evacuation of oven gas to collecting main)	High	Not applicable
		Larry-mounted scrubbers	High	Scrubbers applicable
		Fixed duct secondary collectors with gas cleaning systems (e.g., bag house)	High	Gas cleaning system applicable
		Closed charging systems (tested in PDU scale only)	High	Possibly applicable
Pushing/ Discharging	Particulates, hydrocarbons, ammonia & CO	Bench-mounted self contained hoods with gas cleaning systems	High	Possibly applicable
		Coke car - mounted hoods	High	Gas cleaning system applicable
		Fixed duct hoods with gas cleaning systems	High	Gas cleaning system applicable
		Spray systems	Med.	Applicable
		Coke-side enclosures (sheds) with gas cleaning systems	Med.	Applicable
Quenching	Coke breeze, particulates, organics	Quench tower (containing internal baffles)	Med.	Possibly applicable
		Dry quenching	High	Possibly applicable
		Closed quenching	High	Applicable
Coking	Particulates, hydrocarbons, CO, ammonia & NO_x	Mechanical/Magnetic lid lifters	Unknown	Possibly applicable
		Electrical eye synchronization	Unknown	Possibly applicable
		Oven and door maintenance	Low	Applicable
		Oven/battery sheds	High	Applicable

*High = 90+ %
Medium = 60-80%
Low = 60% or less

Staged Charging--

A slight negative pressure is maintained on the ovens to draw gases from the space above the charged coal into a raw gas collecting main. This practice is call "charging on the main." This negative pressure is provided by a steam jet aspiration system. While the aspirator performs its task, air is drawn into the oven through the charging holes and leveler door. Since air is undesirable when introduced to the gas recovery equipment, the time required for charging is kept to a minimum.

Staged charging also known as "smokeless charging", besides utilizing a steam jet aspirator, incorporates other novel control approaches. The larry car is sealed, air conditioned, and capable of mechanically (magnetic lifter) opening the lids. The coal-containing hopper is lowered over the open oven port as in other systems, but when charging is complete a plug of coal is left in the hopper before the lid is replaced. The charging is done sequentially, filling one side of the oven first then working across to the other side. The advantage of this procedure is the elimination of the sudden burst of emissions from the simultaneous charging of all oven ports. The Clairton Works of United States Steel (U.S.S) was one of the first plants to achieve effective stage charging through personnel training, observation and monitoring. During the period between 1973 and 1977, U.S.S was able to reduce the charging time from 50 seconds down to 6 seconds for equivalent opacity (visible emissions) greater than or equal to 20 percent. This represented an overall reduction of almost 90 percent of the fugitive emissions attributed to charging coke ovens.

In 1973, C.F. & I Steel Co, Pueblo, Colorado initiated sequential (staged) charge techniques which achieved a reduction in visible emissions (greater than 40% equivalent opacity) from 85 seconds per charge to 27 seconds per charge. Additional techniques they employed, such as modification of steam aspiration nozzles and installation and maintenance of hydraulically operated mechanical gooseneck cleaners, have currently reduced the opacity of charging emissions down to 5.8 seconds per charge. This application also represents a greater than 90 percent reduction in visible emissions during the charging operation of a coke oven.

Since staged charging consists of special mechanisms and procedures of coal feeding to the ovens, these techniques do not appear to be applicable to coal conversion systems. Each coal conversion system has its own coal feed/condition which is unique to the given system.

Gas Scrubbers--

Gas scrubbers on larry cars were first introduced in Germany and brought to the U.S. in the late 1960's when tall ovens became popular. In principle, all scrubber cars operate in the same manner. The coal is discharged from the larry car into the oven through a spout and the evolved gases are collected in an annular space around the spout, ignited and cleaned before being discharged to the atmosphere. Wet scrubbers, installed on the larry car, demonstrated a control efficiency for charging emissions by greater than 95 percent for particulates.

The scrubber system associated with this control technology should be applicable to coal conversion systems. However, the capturing devices (e.g., larry car with concentric feed spout and exhaust system), are not applicable.

Fixed-Duct Secondary Collectors--

More recently, the Japanese have installed a fixed-duct, secondary collector and gas cleaning system which are utilized in conjunction with larry car wet scrubbers. Connection ports to a stationary main are provided at each oven to direct the larry car scrubber exhaust to a fixed scrubber and fan for secondary emission control and exhaust to the atmosphere.

Closed-Charging Systems--

The closed-charging system, also known as "pipeline charging," reduces most of the emissions during charging by employing a completely enclosed charging operation. The coal is first crushed, then it is preheated to $500^{\circ}F$ to remove all of the moisture. The dried coal is then stored in a charging bin which is pressurized prior to charging. Afterwards, the coal is introduced into a pipeline which follows the length of a coke oven battery with pipes connecting to each oven along the run on the battery. The pressure in the bin is sufficient to start the coal in motion and its movement is continued by a series of strategically located jets that supply steam at supersonic velocities. These jets permit both upward and forward motion of coal through the pipe. As the coal loses momentum and starts to fall to the bottom of the pipe, another set of steam jets is activated and prevents the disentrainment of the coal. The coal is then directed in the oven which is prepared for charging. Coal can be charged at a rate of 2.5 tons per minute. Since it is partially fluidized, it tends to spread itself evenly throughout the oven obviating the need for a leveling bar. The theoretical control efficiency for this prototype system approaches 100 percent. However, in practice it has been found that emissions evolve from the charging hole lids and the coke oven doors due to the high pressure in the ovens. Closed-charging systems, similar to the type described above, are being used or developed for some coal conversion systems.

Pushing or Discharging Emission Control

After the coal has been coked, it must be pushed from the oven and transported to a quenching station. The pusher is a combination of three machines: a pusher, a leveler and a door extractor. It is designed to operate on an independent track which runs parallel to and independent of the battery. The coke receiving quench car operates on tracks at grade; also, independent of the battery and in the opposite side of the coke oven from the pusher machine. All pushing or discharging emission control systems operate in conjunction with the quench car.

The performance of the pushing/discharging emission control system is extremely sensitive to the condition of the coke when it is pushed. If two important coking cycle variables, oven residence time and homogeneous oven temperature, are not carefully maintained throughout the cycle "green coke" may form. If the coke is pushed in this undesirable condition, no presently developed pushing control system can effectively capture and control the excessive emissions associated with it. The various system control efficiencies, where given, do not presume green coke pushes.

The pushing of the incandescent coke from the oven into the quench car results in emission of hot coke particles and tars, as well as gases as it leaves the oven and is dumped into the quench car. Various systems being developed for pushing emission controls are discussed below.

Bench-Mounted Self-Contained Hoods--

Bench-mounted, self-contained hood systems include designs incorporating mobile hoods, ducts, scrubbers or other high-efficiency control devices, and fans that are mounted on a separate vehicle which traverses the length of the battery on the bench with the coke guide. Utilization of this approach has been confined to West Germany. A mobile version of this gas cleaning system could have application for the coal conversion systems.

Coke Quench Car-Mounted Hoods--

Coke quench car-mounted hood systems include a family of designs employing hoods, ductwork, scrubbers, and fans which are mounted on and travel with, the coke quench car.

Many recent commercial designs of this type of control system have been developed jointly by industry and the EPA. Five different systems are operating or are proposed to go into operation include: Koppers for its own Erie, PA plant and for Bethlehem Steel's coke plants in Johnstown, PA; U.S.S for its Gary Works No. 2 Battery; Dravo for Armco Steel's new battery at Middletown, Ohio; Granite City Steel, Div. of National Steel Corp., and McKee Otto for the Granite City plant; and Chemico Air Pollution Control Co., Div. of Envirotech Corp. for Jones and Laughlin Steel Co.'s Pittsburgh Works. Also, National Steel Corp., for its Brown's Island coke plant, has been operating a closed quench car system for several years. National has started up its system on a coke battery at Armco Steel in Hamilton, Ohio and recently installed a system at the C.F.&I coke plant in Pueblo, Colorado.

The principal features of these designs include a modified door machine with coke guide housing attached, a mechanism to permit the discharge of hot coke, a control car containing gas cleaning equipment, and the operator's cab and quench car with fixed hood. The gas cleaning systems will be applicable to coal conversion systems but the other special design features may not be suitable for coal conversion applications.

Fixed-Duct Hoods--

Fixed-duct hood systems provide a stationary duct, fan, and scrubbing system with duct ports for connecting to a mobile hood arrangement over the pushing operation.

A system of this type commenced operation at the Minister Stein coke plant in Germany in early 1975. The system was designed and constructed by Hartung, Kuhn and Co. and formed the basis of the design of the Allied

Chemical Co. Ashland, Kentucky plant system. This system was furnished by Dravo-Still, in conjunction with Hartung, Kuhn and Co. The Allied Ashland system began operation in the United States in December, 1978.

The Dravo-Still system is a combined mobile and land-based system. The mobile section is made up of two parts. The first part consists of a main quench car hood, a tripper car, a regenerator heat exchanger, a short section of main hood ductwork and a short section of auxiliary ductwork which connects to the coke guide hood ductwork. The second part is the hood and ductwork located on the door machine above and along the sides of the coke guide. The duct from this part is connected to the primary ductwork by a telescoping duct section mounted in the door machine. The main feature of this system consists of the gas transition (tripper) car which travel along the top of a stationary duct placed along side the quench track. The duct possesses a continuous opening along the top which is internally braced and covered with grating to provide support for the belt which seals the opening. The tripper car lifts the belt over the duct inlet section between the tripper rolls and covers the duct opening to convey the gases from the mobile hooding into the stationary duct.

When the system is in operation, emissions are collected simultaneously above the coke guide and quench car and are carried through the stationary duct to the particulate collection equipment, which may be a scrubber, fabric filter or wet electrostatic precipitator. Although no test data are available, preliminary tests have shown favorable results. A similar system is operating successfully at Dominion Foundries & Steel Ltd. (DOFASCO), Hamilton, Ontario in Canada. Three additional systems are under construction which will utilize a fabric filter particulate collection device. These type systems, also known as "smokeless pushing" have been estimated to achieve 95 percent collection efficiency. The gas cleaning system associated with this control technology will be applicable to the coal conversion systems. However the fixed-duct and mobile hood arrangement will probably not be suitable.

Spray Systems--

Water spray or fogging systems can be employed to minimize pushing emissions. Such sprays can be located at the coke guide or the coke quench car. Where sprays alone can be partially effective, they are more often used to enhance the effectiveness of hood and scrubber systems. Electrical safety, ice formation, and water removal are necessary concerns with this type of system. Spray systems will have applications in coal conversion systems in many operations, e.g., dust control from coal storage piles.

Coke-Side Enclosures--

Coke-side enclosures or sheds entail nearly complete enclosure of the coke side of the battery instead of local hooding. Numerous design advantages are cited, which are simplicity of design and operation, ease of retrofitting to existing batteries, and the ability to collect emissions from leaking doors. Since the shed encloses the coke side portion of the battery, some of the coke oven operators working in this area might be exposed to higher emissions. These emissions could subject the workers to additional health hazards.

Enclosures, sheds and hood systems should have applications in coal conversion systems for fugitive emissions control.

Quenching Emission Control

Quenching (wet) in most modern plants is accomplished by receiving the charge of hot coke from the ovens in the quenching car, which is conducted to the quenching station or tower by a locomotive, where the coke is quenched by water.

Quench Tower With Internal Baffles--

The most common methods of reducing particulates and gaseous emissions which rise with the steam evolved from quenching are to trap the pollutants as they ascend through the quench tower, or to reduce the amount of steam generated. Both of these goals are achievable to a limited extent through use of internal baffles, also called "mist suppressors". They are simply different arrangements of wooden slats which are inclined and perpendicular to the path of the rising steam in the tower. As the steam passes through the wooden configurations, particulates tend to become trapped on the wood. Also, some of the steam recondenses on contact with the cooler surface of the baffle.

Recently, the Dominion Foundries & Steel Ltd. at Hamilton, Ontario had tests conducted on their quench tower. The results of the tests which varied quench tower, quench water and mist eliminator conditions gave an average of 0.245 pound of particulate matter per ton of coal charged. Also it was determined that, upon using recycle water for quenching, the emission rate was 0.21 pound per ton of coal charged; and using once-through bay water the average was 0.234 pounds per ton of coal charged. Also, it was found that increasing the baffle angle from 20° to 40° to 30° to 60° had the greatest effect on increasing the collection efficiency. The overall control efficiency was found to be 60 percent for particles greater than 100 microns. Test efficiencies have been reported by others as high as 80 percent.

Also, in tests conducted at the Lorain Works plant of U.S.S aside from particulate matter, organic compounds were also detected. It was found that 10 to 100 pounds per quench of organics, with the bulk identified as aromatics, were being emitted to the atmosphere. These organics are associated with the oil used for controlling the bulk density of the coal charged to the ovens.

Dry Quenching--

Dry quenching involves the use of an essentially inert gas as the heat transfer medium. Heat transfer from the coke to the inert gases is accomplished by direct contact of the gases with the coke. The gases are then conducted through a dust collector to a waste-heat boiler or other type of heat exchanger device.

Plants employing this technique have been operating since 1917, mostly located at town gas plants with the largest handling 1500 TPD. The only existing plant is in Homecourt, France, which cools about 1500 TPD of blast furnace coke. The USSR has developed their own dry quench technology which it has applied to 50 large, new blast furnace coke making facilities, and requires all new and retrofit facilities.

Basically, the system operates in the following manner: incandescent coke is carried to the dry-quenching station in a transfer car, which is raised to the top of the dry-quenching bunker. The hot coke is dumped into the bunker, after which the charging hole then closes and the empty car is returned to the track for another load. As the coke descends the bunker cooling chamber, it is cooled by a counter-current flow of circulating gas. Quench time in the chamber ranges between 2 and 4 hours. At the completion of this cooling cycle, the coke, which has cooled to between 400 and 500°F, is discharged from the bunker through a measuring chamber and double gate arrangement. Except for the periodic introduction of hot coke and a small quantity of air, dry quenching is a closed cycle operation.

Two such systems are presently being marketed by American-Biro Company and Patent Management, Inc. Also, Japanese companies have signed licensing agreements with the USSR and are interested in the potential U.S. market. The Japanese have introduced some modifications to the basic USSR system to achieve greater reliability and improved control efficiency.

Closed Quenching--

There are several types of closed quenching operations which can significantly reduce quenching emissions. One method of approach is to feed hot coke at a controlled rate onto a moving, stainless steel, linear grating in an enclosed operation. As the coke moves along the grating, water is sprayed on it, eventually cooling the coke below combustion temperatures. At the end of the grating, it is then dumped into another container beneath the roof of a kiln. The steam generated is passed through a series of internal baffles which removes most of the particulates. Another advantage of this system, besides controlling emissions, is that a higher quality coke is obtained from the uniform swift cooling.

Closed quenching will be applicable to analogous operations in coal conversion systems, since most of these systems are normally closed and pressurized systems.

Improvements in Operating Procedures and Maintenance

Relatively minor improvements in operating procedures and more subtle approaches to maintenance requirements can significantly reduce emissions from coke oven leaks and openings. These procedures and equipment associated with them would be of use in the coal conversion industry.

Magnetic Lid Lifters--

Until recently many coke plants removed and replaced charging hole lids on top of the coke ovens during charging manually. This method is being replaced by automatic magnetic type lid lifters being installed on the larry cars.

Electric Eye Synchronization--

Electric eyes are being installed on many coke ovens to verify the positioning of the larry car directly over the oven port prior to charging.

Also, they are being used to verify that the door extractor and pushing ram are correctly positioned. They can also be used to properly realign the doors after the push.

Oven and Door Maintenance--

During the coking cycle, excessive emissions may result from poor oven maintenance and from improperly maintained or designed oven doors. Emissions can be significantly reduced by routine scheduling of repair and/or replacement of parts.

An obvious location where significant emissions might occur is the coke oven door. In the past, luted doors were used which required almost continuous luting by workers to prevent emissions. Today, most oven doors are the self-sealing knife edge type. These doors when fitted with appropriate jambs, seals and backstays have demonstrated to be very effective in controlling emissions due to door leakage.

U.S.S has found that through good maintenance and operating procedures, they have achieved 98 percent compliance with a 10 percent door leakage regulatory requirement.

Another significant source of emissions is from the ovens themselves. These emissions tend to increase as the oven battery ages. The Jones and Laughlin Steel Corp. at its Pittsburgh Works found that by silica dusting and patching of its ovens, they were able to achieve a reduction in their coke oven stack emissions of 68 to 87 percent of greater than 20 percent opacity for a period of 6 to 18 minutes per hour.

Recent Control Technology Developments

The Steel Company of Canada (Stelco), Hilton Works in Hamilton, Ontario is operating a fugitive emission control system which employs a shed over the entire coke battery. The shed is capable of capturing 600,000 ACFM of air which is then exhausted to 9 wet-walled electrostatic precipitators. The major drawbacks associated with this type of control system is that the hood exhaust runs constantly and that it tends to corral emissions from the general oven leaks and openings which could adversely affect the battery operators' health. The capital equipment cost for this system is estimated at $7.2 million.

Philadelphia Coke Co., Inc., after consideration of the three basic designs: fixed-duct hood system, coke car-mounted hood system and coke-side enclosures (general descriptions of which were given earlier) favors the fixed-duct hood system for fugitive emission control(65). This system is favored because of the operational and noise problems associated with the coke car-mounted system and the exposure of employees to heavy dust concentrations which would occur within the coke-side enclosure.

Based on blast furnace plants, the estimated cost of the system is in the 4 to 5 million dollar range. Since Philadelphia Coke is a foundry coke plant, which does not experience the dirty pushes (green coke) and high sulfur concentrations in the gas, it is expected the system for foundry coke plants could be installed for about one-half of the above stated costs.

SECTION 8

THE HEALTH EFFECTS OF COKE OVEN EMISSIONS

HEALTH EFFECTS/IMPLICATIONS

To briefly assess the health effects attributed to coke oven emissions, a literature review primarily of recent information released in draft forms by the U.S. EPA - Office of Research and Development was utilized.

The purpose of the review was to provide basic information regarding the potential health effects on coke oven workers and on the general population who are exposed to coke oven emissions.

Chemical Composition of Coke Oven Emissions and their Health Implications

Coke oven emissions consist of all of the constituents of bituminous coal which are released into the atmosphere during the process of coal carbonization. Table 8-1 shows a partial list of the constituents of the coke oven emissions.

A number of these constituents are suspected to be human carcinogens. The toxicity of coke oven emissions may also be associated with respiratory irritation, cocarcinogenesis, tumor promotion and other toxic effects. Table 8-2 summarizes some noncarcinogenic toxic effects.

Particle Size and Its Health Effects

In addition to chemical composition, the form in which the various constituents are released into the atmosphere (e.g., aerosols, gases), and the size and density of the particulate matter with which they are associated determine their effects on human health. Most of the particles emitted are in the respirable range, which means that they can penetrate into the lungs beyond the normal respiratory defense mechanisms. Particles ranging from 0.1 to 2 microns in diameter are the optimum size for such penetration, and therefore, are the most biologically significant. After entering the respiratory tract, they are largely retained in the trachea, bronchi, and alevoli.

TABLE 8-1. PARTIAL LIST OF CONSTITUENTS OF COKE OVEN EMISSIONS (SOURCE: BIBLIOGRAPHY 62)

Anthanthrene
Anthracene
Benzindene
Benz (a) anthracene[b]
Benzo (b) fluoranthene[b]
Benzo (ghi) fluoranthene[b]
Benzo (j) fluoranthene
Benzo (k) fluoranthene
Benzofluorene
Benzo (a) fluorene
Benzo (b) fluorene
Benzo (c) fluorene
Benzophenanthrene
Benzo (ghi) perylene
Benzo (a) pyrene[b]
Benzo (e) pyrene[b]
Benzoquinoline
Chrysene
Coronene
Dibenz (ah) anthracene[b]
Dibenzo (ah) pyrene[b]
Dihydroanthracene
Dihydrobenzo (a) fluorene
Dihydrobenzo (b) fluorene
Dihydrobenzo (c) fluorene
Dihydrobenz (a) anthracene
Dihydrochrysene
Dihydrofluoranthene
Dihydrofluorene
Dihydromethylbenz (a) anthracene
Dihydromethlybenzo (k and b) fluoranthenes
Dihydromethylbenzo (a and e) pyrenes
Dihydromethylchrysene
Dihydromethyltriphenylene
Dihydrophenanthrene
Dihydropyrene
Dihydrotriphenylene
Dimethylbenzo (b) fluoranthene
Dimethylbenzo (k) fluoranthene
Dimethylbenzo (a) pyrene
Dimethylchrysene
Dimethyltriphenylene
Ethylanthracene
Ethylphenanthrene
Fluoranthene
Fluorene
Indeno (1,2,3-cd) pyrene
Methylanthracene
Methylbenz (a) anthracene
Methylbenzo (a) pyrene
Methylbenzo (ghi) perylene
Methylchrysene
Methylfluoranthene
Methylfluorene
Methylphenanthrene
Methylpyrene
Methyltriphenylene
Octahydroanthracene
Octahydrofluoranthene
Octahydrophenanthrene
Octahydropyrene
Perylene
Phenanthrene

o-Phenylenepyrene

Pyrene

Triphenylene

POLYNUCLEAR AZA-HETEROCYLIC COMPOUNDS[a]

Acridine
Benz (c) acridine[b]

TRACE ELEMENTS[b]

Arsenic
Beryllium

TABLE 8-1. (continued)

Dibenz (a,h) acridine
Dibenz (a,j) acridine

AROMATIC AMINES[b]

α-Naphthylamine
β-Naphthylamine

OTHER AROMATIC COMPOUNDS

Benzene[b]
Phenol[c]
Toluene[d]
Xylene[d]

Cadmium
Chromium
Cobalt
Iron
Lead
Nickel
Selenium

OTHER GASES

Ammonia[c]
Carbon disulfide[c]
Carbon monoxide[c]
Hydrogen cyanide[c]
Hydrogen sulfide
Methane[c]
Nitric oxide[d]
Sulfur dioxide[c]

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[a] Lao et al (1975), except as noted.

[b] Kornreich (1976).

[c] Smith (1971).

[d] White (1975).

TABLE 8-2. SOME TOXIC CONSTITUENTS OF COKE OVEN EMISSIONS AND SOME OF THEIR TOXIC PROPERTIES (SOURCE - BIBLIOGRAPHY 62)

Constituent	Suggested Threshold Limit Value (TLV)	Potential Health Effect
Acetone	1,000 ppm 2,400 mg/m^3	At 300 ppm -- Slight irritation 500 ppm -- Still tolerated 1,000 ppm -- Chronic irritation of respiratory tract, dizziness
Ammonia	25 ppm 18 mg/m^3	1 ppm -- Odor detectable 20 ppm -- Discomfort in uninured workers, complaints 100 ppm -- Irritation of respiratory tract and conjuctivae
Acridine		Powerful irritant: eyes Photosensitizer Causes dermatitis
Anthracene		Irritant: eyes, skin, respiratory tract Photosensitizer
Arsenic	0.25 mg/m^3	Contact dermatitis and sensitization Conjunctivitis Ulceration and perforation of nasal septum
Benzene	1.0 ppm/3.0 mg/m^3	Narcotic effects Severe exposures cause bone marrow and blood changes Myelotoxic 25 ppm -- Exposure for 12 years; very little intoxication reported 60 ppm -- Blood changes reported 100-200 ppm -- Deaths reported

TABLE 8-2 (continued)

Constituent	Suggested Threshold Limit Value (TLV)		Potential Health Effect
Beryllium	0.002 mg/m^3		Dermatitis, tracheobronchitis
		100 μg/m^3 --	pneumonitis
Cadmium dust	0.05 mg/m^3		Distinctive, nonhypertropic emphysema, with or without damage to renal tubes; anemia, eosinophilia, anosmia, chronic rhinitus, yellow ring on teeth, bone changes
		2-15 mg/m^3 --	Anosmia, proteinuria (low molecular weight) pulmonary emphysema, yellow ring on teeth, eosinphilia, anemia
Chromium	0.5 mg/m^3		Dermatitis (salt)
Cobalt	0.01 mg/m^3		Pulmonary involvement, chronic interstitial pneumonitis
		1-2 mg/m^3 --	Serious and occasionally fatal results, hypersensitivity, allergic dermatitis
Formaldehyde	2 ppm		Irritant: eyes, respiratory tract, skin
		1-2 ppm --	Itching eyes, dry and sore throat, disturbed sleep, unusual thirst on awakening
		6 ppm --	Eye irritation
Hydrogen Cyanide	10 ppm	20-40 ppm --	Slight intoxication, variety of neurological symptoms

TABLE 8-2 (continued)

Constituent	Suggested Threshold Limit Value (TLV)	Potential Health Effect
Hydrogen sulfide	10 ppm (15 mg/m^3)	500-1,000 ppm -- Acts primarily as systematic poison causing unconsciousness and death through respiratory paralysis.
		50-500 ppm -- Acts primarily as a respiratory irritant.
		250-600 ppm -- Prolonged exposure may lead to pulmonary edema and bronchial pneumonia.
		5-100 ppm -- Associated with eye irritation.
Lead	0.15 mg/m^3	Nerve function disorders, inability to sleep, fatigue, constipation; Long-term exposure: anemia, colic, neuritis, headaches, loss of appetite, weakness, double vision: Organic lead: mental disturbances, inability to sleep, general anxiety, delerium - acute.
Nickel	1 mg/m^3	Increase in incidence of nasal, sinus, and lung cancer in workers in nickel refineries
Pyridine	5 ppm	0.83-2.46 ml -- Was toxic in human therapy with one death from liver and kidney damage. Central nervous system affected. Stimulates bone marrow to production of blood platelets . Vapor - irritating to mucous surfaces.
		15-330 ppm -- Nausea, headache, insomnia and nervousness, low back or abdominal discomfort.

TABLE 8-2 (continued)

Constituent	Suggested Threshold Limit Value (TLV)	
Selenium	0.2 mg/m^3	Intense irritation of eyes, nose, and throat, headache. Severe exposure: bronchial spasma, asphyxiation, chills, fever, bronchitis. 0.007-0.05 mg/m^3 -- Headache, traecheobronchitis, conjunctivitis. 0.2-0.4 mg/m^3 -- Garlic odor of breath, skin rashes, indigestion, metallic taste.
Sulfur dioxide	5 ppm 13 mg/m ^{3}	Irritation of the mucous membranes, coughing, eye irritation, increased pulmonary flow resistance; adverse symptoms appear at levels between 5 and 10 ppm.
Toluene	100 ppm 375 mg/m^3	100-1,100 ppm -- Enlargement of liver, macrocytosis, moderate decrease in erythrocyte count and absolute lymphocystosis. 200 ppm -- Headache, nausea, lassitude. 200-500 ppm -- Impairment of coordination, momentary loss of memory, anorexia. 500-1,500 ppm -- Palpitation, extreme weakness, pronounced loss of coordination and impairment of reaction time; red cell decrease in 2 cases, aplastic anemia (possible benzene impurity); 200 ppm -- Slight but definite changes in muscular coordination; 7 hours exposure to 200 ppm cause prolongation of reaction time, decreases in pulse and systolic blood pressure.
Xylene	0.1 mg/m^3	Acute oral and skin irritation, sensitization, gastrointestinal irritant.

Particles larger than 2.0 microns are trapped by the mucous membranes and do not enter the lungs. Particles smaller than 0.1 micron are retained in the tracheobronchial tree but elution does not occur. Particles smaller than 0.04 micron do not come out of suspension in the inhaled air and are exhaled. The trapped particles in the mucus that are not exhaled and that also do not enter the lung are either swallowed or spit out. Table 8-3 gives the range of particle sizes found in coke oven emissions.

Synergisms

Some researchers have shown the importance of synergism of pollutants in air, two of the most common being sulfur dioxide (SO_2) and benzo-a-pyrene (BAP). It has been postulated that SO_2 synergism shows ciliary action, and therefore increases BAP retention and/or causes chronic injury; following injury, the resultant regenerating cells may be more susceptible to the BAP. These effects have also been demonstrated between carcinogenic chemicals (e.g. BAP) and particulate matter (e.g., iron oxide, carbon).

The indication in laboratory experiments that different components of coke oven emissions interact synergistically lends support to the view that the toxic potential of the complex mixture -- coke oven emissions -- cannot be related to the potential of a single compound.

BASIS OF SAMPLING AND MEASUREMENTS

Because of the effort and complexity that would be required in characterizing all of the constituents of coke oven emissions, various surrogate measures have been used in the past. These usually are of three types:

Total Suspended Particulates	(TSP)
Benzene Soluble Organics	(BSO)
Benzo (A) Pyrene	(BAP)

TSP is generally considered not to be a specific enough measure for assessing total occupational health effects. Previous occupational and general atmospheric studies provide some justification for using a surrogate measure rather than trying to identify and control each of the polynuclear aromatic (PNA) compounds emitted by coke ovens.

Table 8-4 summarizes the exposures of coke oven workers to coke oven emissions (benzene soluble fraction of total particulates).

TABLE 8-3. PARTICLE SIZE RANGE AND BIOLOGICAL SIGNIFICANCE OF COKE OVEN EMISSIONS (SOURCE - BIBLIOGRAPHY 62)

Size[a]	Site	Process	Reference	Biological significance
0.1-1 µm (tarry droplets)	Retort house		Lawther (1964)	Particles in the 0.1-2.0 µ range are respirable and largely retained in the trachea, bronchi, and alveoli. Particles > 2.0 µ are trapped in the mucous membranes. Particles < 0.1 µ are retained but elution does not take place. Particles < 0.04 µ are exhaled (Falk and Kotin, 1961).
1 µm and up (dust)	Retort house		Lawther (1964)	
1.5 µm	Topside coke oven	General atmosphere (shift change)	White, L.D. et al[b]	
1.8 µm	Topside coke oven	During coking	White, L.D. et al[b]	
2.9 µm	Topside coke oven	Charging	White, L.D. et al[b]	
1 µm -1.27 mm	Coke plant	Quenching	Fullerton, R.W. (1967)	
5 µm -1.27 mm	Coke plant		Masek, V. (1970, 1970a)	

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[a] For respirable particles, the rate of elution of PAH increases with the size of the particle to which the PAH is absorbed.

[b] No date.

TABLE 8-4. SUMMARY OF EXPOSURES OF COKE OVEN WORKERS TO COKE OVEN EMISSIONS (BENZENE SOLUBLE FRACTION OF TOTAL PARTICULATES)

[SOURCE - BIBLIOGRAPHY 32]

A Summary of Separate Air Sampling Studies by AISI Member Companies and Pennsylvania Department of Environmental Resources.

Operator (source of info.)	No. of Samples	Range* (mg/m^3)	Average** (mg/m^3)
Larry car operator			
AISI	106	0.78 - 6.4	2.2
PA	39	0.28 - 8.8	3.1
Lidman			
AISI	140	1.0 - 5.6	2.6
PA	61	0.42 - 18.	3.2
Door Machine Operator			
AISI	85	0.31 - 5.1	1.2
PA	25	0.04 - 6.5	2.1
Door Cleaner/Luterman			
AISI	172	0.31 - 3.2	1.1
Patcher			
AISI	10	0.71 - 1.3	0.99
Heater			
AISI	60	0.12 - 2.4	0.57
PA	39	N.D. - 3.0	1.1
Quench Car Operator			
AISI	70	0.05 - 1.2	0.44
PA	23	N.D. - 7.0	0.94
Pusher Operator			
AISI	78	0.15 - 0.82	0.40
PA	23	N.D. - 0.93	0.39

* AISI DATA is a range of the mean coke oven emission concentration reported for each job description by each coke plant studied.

** AISI DATA is the average of mean concentration for each coke plant studied.

N.D. - None Detected.

Table 8-5 shows a comparison of BAP concentrations measured at coke oven batteries and at other selected sites.

The National Air Sampling Network (NASN) routinely monitors suspended particulate levels in urban and non-urban areas. BAP and BSO are monitored for 40 locations that include cities with and without coke ovens and rural areas (See Table 8-6). The BAP concentrations are generally 0.1 ng/M^3 for rural locations. Most urban locations without coke ovens have average concentrations of less than 1 ng/M^3 (the average is 0.38 ng/M^3); however, areas with coke ovens generally have average concentrations in excess of 1 ng/M^3 (the average is 1.21 ng/M^3).

EPIDEMIOLOGICAL STUDY RESULTS

Epidemiological evidence of greater increases in disease rates among workers exposed to the higher-temperature processes suggests that the higher the temperature of carbonization, the higher the proportion of toxic compounds released. Table 8-7 shows the excess of reported lung cancer among workers for various carbonizing chamber temperature ranges.

Epidemiological studies in different countries have demonstrated that workers exposed to the products of combustion and distillation of bituminous coal experience an increased incidence of cancer of several sites (lung, pancreas, kidney, bladder, skin). Table 8-8 is a summary of relative risks of death from cancer among coke oven workers.

There are no epidemiological studies of the cancer exposure of populations living near coke ovens or gas works. As a basis for estimating the magnitude of the excess cancer risk, the summary was extrapolated from cancer mortality data on coke oven workers and other workers in the steel industry.

Because the extensive epidemiological evidence describes adverse health effects experienced by an industrial work force exposed to "coke oven emissions" (i.e., the total, complex mixture, often characterized as the benzene-soluble fraction of total particulate matter), the effects of the constituents such as BAP and BSO acting separately or in various combinations need not be delineated for human experience. It is, therefore, essential that the assessment of health effects be applied to "coke oven emissions" as an entity and not to any particular component.

TABLE 8-5. COMPARISON OF BENZO (a) PYRENE CONCENTRATIONS MEASURED AT COKE OVEN BATTERIES AND AT OTHER SELECTED SITES

(BIBLIOGRAPHY 62)

		Concentration. (μg/m^3)			
Country	Year	Top-Side		Side	
Soviet Union	1962	1.27 - 27.4			
Soviet Union	1968	0.05 - 7.38	(3.84)[a]	0.08 - 0.27	(0.17)
Japan	1968			1.5 - 3.14	
Norway	1959	2 - 7.3			
Czechoslovakia	1966	1.1 - 94.8			
Czechoslovakia	1967	3.6 - 32.2			
Czechoslovakia	1968	10.7 - 12.7		0.6 - 3.4	
Czechoslovakia	1974	0.1 - 13.1			
England	1965	3 - 216			
USA	1974	1.2 - 15.9	(6.5)	0.3 - 1.98	(1.0)
USA	1960	8.3 - 51			
USA	1974	0 - 225.9	(9.55)		
USA	1974	0.18 - 36.3	(5.78)		
				Contrast	
USA	1968	95		Cigarette smoke	
USA	1961	6.1		Auto exhaust	
USA	1961	14 - 78		Roof tarring	
Switzerland	1961	640		Roof tarring	
USSR	1966	13.7 - 22		Aluminum Plant	
England	1965	(0.02)		Urban - London	
England	1965	2,330		Maximum found in fumes emitted from coke ovens	
USA	1959	(0.022)		Birmingham	
USA	1966	(0.0185)		Birmingham	

[a] Mean.

Source: White, et al.

TABLE 8-6. AMBIENT BAP AND BSO DATA (SOURCE - BIBLIOGRAPHY 64)

Pollutant	Statistic	Cities with Coke Ovens	Cities without Coke Ovens	Rural Areas
BAP (ng/m^3) 1975 Data	Average	1.21	0.38	<0.10
	Sample size	21.00	13.00	3.00
	Range	0.3 - 4.7	0.03 - 0.9	<0.10
BSO (μg/m^3) 1971-72 data	Average	4.21	3.75	0.95
	Sample size	25.00	12.00	2.00
	Range	2.1 - 7.3	1.9 - 5.6	0.8 - 1.1

TABLE 8-7. TEMPERATURE RANGE OF CARBONIZING CHAMBERS AND EXCESS OF LUNG CANCER REPORTED. (SOURCE - BIBLIOGRAPHY 62)

Carbonizing Chamber	Temperature Range, °C	Reported Excess of Lung Cancer among Workers (%)
Vertical retorts	400 - 500	27 (Doll, 1965)
Horizontal retorts	900 - 1,100	83 (Doll, 1965)
Coke ovens	1,200 - 1,400	255 (Lloyd, 1971)
Japanese gas generators	≥ 1,500	800 (Lloyd, 1971)

TABLE 8-8. SUMMARY OF RELATIVE RISKS OF DEATH FROM CANCER AMONG COKE OVEN WORKERS[a]
(SOURCE - BIBLIOGRAPHY 62)

Length of employment (1953-1970), yr	Distribution of workers			Deaths and RR's of death from malignant neoplasms						Deaths and RR's of death from respiratory cancer					
	5+	10+	15+	5+		10+		15+		5+		10+		15+	
Work area				Obs.	RR	Obs.	RR	Obs.	RR	Obs.	RR	Obs.	RR	Obs.	RR
Total coke oven	1860	1194	790	166	1.47^{b}	136	1.50^{b}	108	1.62^{b}						
Coke oven	993	574	325	101	1.66^{b}	85	1.95^{b}	63	2.40^{b}	54	3.02^{b}	44	3.42^{b}	33	4.14^{b}
Oven topside full-time	150	72	29	35	3.70^{b}	22	5.12^{b}	12	7.63^{b}	25	9.19^{b}	16	11.79^{b}	8	15.72^{b}
Oven topside full-time	290	245	159	26	1.59^{b}	31	1.85^{b}	32	2.73^{b}	12	2.29^{b}	16	3.07^{b}	18	4.72^{b}
Oven side only	553	257	137	40	1.17	32	1.46	19	1.51	17	1.79^{c}	12	1.99^{b}	7	2.00
Non-oven	836	578	392	65	1.28	48	1.10	39	1.13						
No one coke plant area	31	42	73	0	d	3	d	6	1.34						

	Deaths and RR's of death from cancer of digestive system among non-oven workers					
	5+		10+		15+	
	Obs.	RR	Obs.	RR	Obs.	RR
All malignant neoplasms of digestive system	28	1.58^{c}	23	1.53	19	1.53
Large intestine	11	2.31^{c}	10	2.52^{b}	8	2.37^{c}
Pancreas	8	3.67^{b}	7	3.75^{b}	6	4.29^{b}
Other	9	0.83	6	0.65	5	0.65

[a] Adapted from Redmond (1976).
[b] $p<0.01$. $p < 0.01$
[c] $p<0.05$. $p < 0.05$
[d] less than 5 deaths.

Several mortality studies have shown that workers at coke plants are at an increased risk for dying of chronic bronchitis. Unlike the risks from respiratory malignancy, the risk appears to be about the same for coke oven workers and for non-oven workers employed at the plant. It indicates that the risk of the plant workers is greater than two-fold relative to the rate of mortality from chronic bronchitis in the steelworker population. Table 8-9 shows the estimated effects of coke oven emissions on U.S. population. An affected radius of 15 kilometers (approximately 9 miles) from a coke plant is considered as the maximum potential exposure population. The estimate indicates that for the highest 100,000 people exposed there is a 0.2 to 0.6 percent excess chance of dying of lung cancer. For the remaining 15 million people, the excess is about 0.1 percent. The total number of excess lung cancer deaths is about 150 cases per year. These estimates should be regarded as crude and probably conservative; i.e., on the high side.

Without any significant coke oven exposure, the lifetime probability of dying of lung cancer is 3.29 percent.

SUMMARY OF STUDY FINDINGS

- Exposure to coke oven emissions provides an elevated risk for cancer of all sites and non-malignant respiratory diseases to coke oven workers and an increased risk among lightly exposed workers (non-oven workers in coke plant).
- The general population, which includes the young, the old and the infirm in the vicinity of a coke oven plant should be considered more susceptible than the workers, especially for development of chronic bronchitis, since they are generally in poorer health.
- Coke oven emissions contain an array of identified carcinogens, irritants, particulate matter, trace elements, and other chemicals. The toxic effects observed in both humans and animals are greater than the effects that can be attributed to any individual component. Thus "coke oven emissions" as a whole should be considered the toxic agents.
- There is an exposure difference of about 2 orders of magnitude estimated between lightly exposed workers and people living in the vicinity of a coke plant. Since these lightly exposed workers show

an elevated risk for cancer and non-malignant respiratory disease, it is reasonable to assume that levels up to one-hundreth of those to which lightly exposed workers are subjected could cause an increased risk to the general population.

TABLE 8-9. ESTIMATED EFFECTS OF COKE OVEN EMISSIONS ON U.S. POPULATION UNDER WEIBULL PROBABILITY MODEL WHERE "HIT PARAMETER" m = 1 AND ADJUSTMENTS FOR TOTAL POPULATION RATES USED

(SOURCE: BIBLIOGRAPHY 1)

X = Exposure to BSO in μg/m^3 in Air	Number of People in Exposure Group	Lifetime Probability of Lung Cancer	Increase in Lung Cancer Due to Coke Oven Emissions	Given Coke Oven Emissions Caused Lung Cancer Average Yrs. of Lifespan Lost	No. of Lung Cancer Deaths/Yr. Due to Coke Oven Emissions
Background= 3.75	-	.03286	-	-	-
4.50	13,900,000	.03360	6.37×10^{-4}	12.34	125.0
5.50	1,034,000	.03435	1.49×10^{-3}	12.36	22.0
6.50	54,000	.03519	2.33×10^{-3}	12.39	1.8
7.50	7,780	.03604	3.18×10^{-3}	12.41	.4
8.50	2,420	.03669	4.02×10^{-3}	12.43	.1
10.90	1,800	.03890	6.04×10^{-3}	12.44	.2

Total=149.5/Yr.

SECTION 9

ENVIRONMENTAL REQUIREMENTS IN THE COKE OVEN INDUSTRY

The section discusses existing and proposed Federal and State laws, rules and regulations pertaining to environmental control in the coke oven industry. It is not intended to represent all applicable regulatory requirements, particularly with respect to water quality standards, due to their variations from state to state.

FEDERAL REGULATIONS

Air Pollution Control Standards

1. Prevention of Significant Air Quality Deterioration (PSD) program was incorporated in the Federal Clean Air Act Amendments of 1977 (PL 95-95, August 7, 1977) under Part C, Subpart I.

   This regulatory program requires that every major new and major modification of industrial sources of air pollution must obtain a PSD permit in order to construct the source or facility. A major source is any source in one of 28 established categories that has the potential (before controls) to emit 100 tons per year (approximately 25 lbs/hr) or more of any pollutant regulated by the Clean Air Act.

   Included in the 28 major source categories are: coke oven batteries, fuel conversion plants and sulfur recovery plants, which are pertinent to this study report. The regulated pollutants presently include: particulate matter, SO_2, NO_x, CO, hydrocarbons, photo-chemical oxidants, total flourides, sulfuric acid mist, asbestos, beryllium, mercury, vinyl chloride, benzene and lead.

The requirements for obtaining a PSD permit are:

A. Air Quality Assessment

A permit application must be accompanied by an air quality assessment that satisfactorily demonstrates that no increment or NAAQS will be contravened. This assessment must be based on approved air pollutant dispersion modeling techniques and, in the case of the NAAQS, must be supported by as much as one year's worth of monitoring data.

B. Best Available Control Technology (BACT)

BACT is the best achievable control technology when economic, energy and other costs are considered on a case-by-case basis. BACT can range from the stringency of Lowest Achievable Emission Rate (LAER) down to the New Source Performance Standards (NSPS) as the highest acceptable emission rate.

If any control technology less than the best achievable is selected, then that selection must be justified by a comparison between the economic and energy cost saved and the additional environmental cost accrued.

BACT is required for all pollutants for which the new source or modification is considered major.

C. Impact Analysis and Public Participation

Addressed in the permit application must be the impact on: vegetation with commercial or recreational value, soils and visibility. Also the impact in the environment of secondary or induced growth must also be evaluated.

The public must be afforded an opportunity for comment and hearing on the permit application; and in the preliminary determination to approve the application prior to issuing a construction permit.

D. New Sources in Non-attainment Areas

All major new sources or major modifications proposed for location in areas where levels of any pollutant (for which they are considered major emitters) are currently exceeding a NAAQS must meet the following four conditions in order to secure a state Stationary Source Review (SSR) permit (a precondition to receiving a PSD permit).

1. LAER is required.
2. All other sources owned by the same owner in the same state must be in compliance with the SIP or on an approved compliance schedule.
3. Off-setting reductions in emissions from existing sources must be provided.
4. There must be a net improvement in air quality resulting from the off-sets.

2. Standards of Performance for New Stationary Sources have not been written for the coke oven industry. Instead, the EPA* has been considering emission standards for various coke making operations under the National Emission Standards for Hazardous Air Pollutants (NESHAPS 40 CFR 61). The purpose of promulgating regulations under this category is to provide an umbrella coverage of new and existing coke plants while acknowledging the carcinogenic properties of the contaminants. It is anticipated that the EPA will propose an initial regulation to control the top side charging of coke ovens by visible emission limitations. Also, it is expected that specific emission standards will be set for benzene and heavier polycyclic aromatic hydrocarbons which will be applicable to the coke oven industry.

3. National Primary and Secondary Ambient Air Quality Standards (40 CFR 50). Table 9-1 provides ambient air quality standards for six major air contaminants. These standards serve as guidelines to the states

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*Private communications with EPA, Standards Group, R.T.P., North Carolina. Also, the Precip Newsletter - March 20, 1978, No. 26, page 4.

TABLE 9-1. NATIONAL AMBIENT AIR QUALITY STANDARDS (SOURCE - BIBLIOGRAPHY 19)

Pollutant	Averaging Time	Primary Standards	Secondary Standards
Particulate matter*	Annual (geometric mean)	75 μg/m^3	60 μg/m^3
	24 - hour	260 μg/m^3	150 μg/m^3
Sulfur dioxide	Annual (Arithmetic mean)	80 μg/m^3 (0.03 ppm)	
	24 - hour	365 μg/m^3 (0.14 ppm)	
	3 - hour		1,300 μg/m^3 (0.5 ppm)
Carbon monoxide	8 - hour	10 mg/m^3 (9 ppm)	Same as primary
	1 - hour	40 mg/m^3 (35 ppm)	
Photochemical** oxidants	1 - hour	235 μg/m^3 (0.12 ppm)	Same as primary
Hydrocarbons+ (nonmethane)	3 - hour (6 to 9 a.m.)	160 μg/m^3 (0.24 ppm)	Same as primary
Nitrogen dioxide	Annual (Arithmetic mean)	100 μg/m^3 (0.05 ppm)	Same as primary
Lead	3 - month average	1.5 μg/m^3	Same as primary

* The secondary annual standard (60 μg/m^3) is a guide to be used in assessing implementation plans to achieve the 24 - hour secondary standard.

** Expressed as ozone by the Federal Reference Method.

+ This NAAQS is for use as a guide in revising implementation plans to achieve oxidant standards.

for meeting air quality goals by incorporating them in their State Implementation Plans. National standards apply when state standards of equivalent or more stringent levels have not been adopted.

Water Pollution Standards

1. Refuse Act of 1899 (33 USC 407); NPDES permit.

   This act makes unlawful the discharge of refuse into navigable waters or tributaries of navigable waters; or the deposit of refuse on the banks of navigable waters where it may be washed into those waters. Discharges may, however, be permitted under the National Pollution Discharge Elimination System (NPDES) pursuant to the Federal Water Pollution Control Act Amendments of 1972 (33 USC, 1251 et. seg.).

2. Toxic Pollutant Effluent Standards (40 CFR 129).

   The pollutants presently regulated by these standards are not related to the coke oven industry effluent compounds. It is expected that pollutants characteristic of the effluents from the coke oven industry such as particulate polycyclic aromatic hydrocarbons, benzene, metals and heavy metals will be proposed and regulated in the near future.

3. Effluent Guidelines and Standards (40 CFR 420) Subpart A; Byproduct Coke Subcategory.

Basis	Effluent Characteristic	Maximum for Any One Day	Avg. of Daily Values For 30 Consecutive Days Shall Not Exceed
BATEA[1], NSPS[1] (Expressed as kg/kkg) Product	Cyanide A[2]	.0003	.0001
	Phenol	.0006	.0002
	Ammonia	.0126	.0042
	Sulfide	.0003	.0001
	Oil and grease	.0126	.0042
	TSS	.0312	.0104
	pH	Within the range from 6.0 - 9.0	

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[1] Limitations specified may be exceeded up to 25 percent by those facilities equipped with gas desulfurization units and up to 70 percent for those utilizing the indirect ammonia recovery process.

[2] "Cyanide A" means those cyanides amenable to chlorination.

EPA Water Quality Criteria

States are required to adopt water quality standards and a plan for enforcement and implementation consistent with the goals of the Federal Water Pollution Control Act Amendments of 1972 (40 CFR, Part 120).

Recognized versions of water quality criteria include criteria developed by the Department of Interior in 1968, criteria published by the National Academy of Sciences in 1972, and EPA's 1976 Quality Criteria for Water. States may use any one of these criteria documents as guidelines in setting discharge standards.

It should be understood that water quality criteria do not have direct regulatory use, but are used for judgment of certain standards associated with water quality programs.

Criteria pertinent to the coke oven industry taken from the proposed EPA 1976 Quality Criteria for Water are presented below:

Parameter	Criterion
Ammonia	0.02 gm/l (as un-ionized ammonia) for freshwater aquatic life.
Cyanide	5.0 μg/l for fresh and salt water aquatic life and wildlife.
pH	5-9 for domestic water supplies (Welfare) 6.5 - 9.0 for freshwater aquatic life 6.5 - 8.5* for saltwater aquatic life *but not more than 0.2 units beyond the normally occurring range.
Phenol	1 μg/l for domestic water supply (Welfare), and to protect against tainting of fish flesh.
Solids & Turbidity	For freshwater fish and other aquatic life settleable and suspended solids should not reduce the depth of the compensation point for photosynthetic activity by more than 10 percent from the seasonally established norm for aquatic life.

Parameter	Criteria
Oil & Grease	Virtually free from oil and grease, particularly from the tastes and odors that emanate from petroleum products, for domestic water supplies. The following apply for Aquatic Life; (1) Levels of individual petrochemicals in the water column should not exceed 0.01 ppm of the lowest continuous flow 96-hr. LC_{50} to several important marine species, each having a demonstrated high susceptibility to oils and petrochemicals; (2) Levels of oils or petrochemicals in the sediment which cause deleterious effects to the biota should not be allowed; (3) Surface waters shall be virtually free from floating non-petroleum oils of vegetable or animal origin, as well as petroleum derived oils.
Sulfide-- Hydrogen Sulfide:	2 g/l undissociated H_2S for fish and other aquatic life in fresh and marine water.

Solid Waste Disposal Standards

The Resource Conservation and Recovery Act of 1976 stipulated that within 18 months[1] regulations would be developed by the EPA to handle and dispose of hazardous waste materials. Since many of the particulates that are captured from the coke ovens are, or could be, classified as hazardous compounds, they would fall under the requirements of this law and the proposed regulations. It is expected that the regulations will require safe handling, labeling and identification of the hazardous materials, proper containerizing, safe and effective transport, and disposal.

[1] (NOTE: Recent conversations with the EPA indicate that the 18 months deadline are expected to be extended an additional 6-12 months.)

STATE REGULATIONS

Air Pollution Control Standards

An analysis was made of five (5) states which specifically regulate coke oven plants and their air emissions. These states collectively encompass more than 37 percent of the total coke production and have more than 41 percent of the total number of coke plants in the United States.

Basically, the states all regulate the fugitive smoke and particulate matter emissions that emanate from the coke oven batteries and the quench towers. The following are the types of operations and maintenance procedures regulated:

1. Unloading and Transferring of Coal and Coke - These operations are required to implement unspecified but reasonable control measures to prevent emissions.
2. Charging Operations -
    - a) Open Charging - Visible emissions are limited to no more than 15 seconds during any coke oven charging operation. The opacity of the emissions is limited to less than or equal to 30 percent.
    - b) Closed Charging - Visible emissions are limited to one charge out of any ten consecutive charges.
3. Pushing Operations -
    - a) Visible emissions are limited to less than, or equal to, 20 percent opacity for up to one minute per push. New coke plants shall be equipped with enclosed pushing devices equipped with particulate collection systems.
4. Topside emissions -
    - a) Leaks shall be wet-sealed or the oven shall not be recharged until repairs are made.
    - b) At no time shall there be leaks in more than 5 percent of the off-take piping and no more than 2 percent from the charging hold lids on any one battery, excluding visible emissions from open standpipe caps.
5. Coke Oven Door Emissions -
    - a) Visible emissions are restricted to 15 percent of the doors on any battery at any time.

b) Self sealing doors must be repaired prior to subsequent charge if they fail to seal.

c) Luted doors that fail to seal after charging must be reluted promptly.

d) Operators must have facilities to maintain and repair coke doors with maintenance inventory of one door per 12 ovens operated.

6. Oven Maintenance -

a) Ovens shall be maintained in good condition.

b) Oven cracks are to be sealed as doon as practicable following detection.

c) Records are to be retained on maintenance of doors, burners and interiors.

7. Combustion Stacks -

a) Visible emissions are limited to less than or equal to, 20 percent opacity except for 3 minutes in any consecutive 60 minutes.

8. Quenching -

a) Quench towers must have baffles installed.

b) Water introduced to the quench station must have a quality approved by the control agency.

New Byproduct coke oven batteries must be equipped with control equipment such as, but not limited to, hood(s) and/or gas mover(s) capable of capturing, containing and collecting gases and particulate matter resulting from distillation, charging, pushing and quenching of coke from an oven battery. Such equipment shall employ the best practicalbe control technology currently available.

New Beehive coke ovens are either prohibited from construction and operation or, if permitted to be constructed, must have all gas and particulate matter emissions directed through an acceptable air pollution control device.

Table 9-2, "Summary of State Air Pollution Control Regulations for the Control of H_2S Emissions from Byproduct Coke Ovens," gives the limitations from five states which regulate the emission of sulfur compounds (measured as H_2S) from coke oven gas. The majority of these states require that the coke oven gas be desulfurized down to 50 grains per one hundred dry standard cubic

TABLE 9-2. SUMMARY OF STATE AIR POLLUTION CONTROL REGULATIONS FOR THE CONTROL OF H_2S EMISSIONS FROM BYPRODUCT COKE OVENS

State	Regulations	H_2S/SO_x Limitations
Alabama	Chap. 5 - Control of sulfur oxides, 5.5 Process Industries - General	1. Cannot construct or operate unless source meets applicable New Source Performance Standards (NSPS) and utilize best practicable control technology currently available. (BPCTCA) 2. Cannot exceed primary & secondary National Ambient Air Quality Standards (NAAQS) for SO_x
Illinois	Rule 204 (f) Sulfur standards and limitations for process emissions sources (1) Sulfur Dioxide and Limitations	(A) Sulfur dioxide emissions from process sources cannot exceed 2,000 ppmv.
New York	New York contaminant emissions from Ferrous Jobbing Foundries and Byproduct coke oven batteries, Part 214, Byproduct coke oven batteries, Sections 214.4 Sulfur Compound Emissions	Sources are not permitted to burn or flare process gas containing more than 50 grains of sulfur compounds (measured as H_2S) per 100 standard cubic feet of gas.
Pennsylvania	Chapter 123, 123.2 Byproduct coke oven gas	a) Coke oven gas must be burned prior to emission to atmosphere. b) Burning or flaring is prohibited if Byproduct gas contains more than 50 grains of sulfur compounds per 100 dry standard cubic feet of gas (expressed as equivalent hydrogen sulfide).

TABLE 9-2 (Continued)

State	Regulations	H_2S/SO_x Limitations
Virginia	Emission standards for coke ovens and charcoal kilns (Rule EX-4) Part IV 4.91 other Byproduct coke ovens emission standards for gaseous pollutants (Rule EX-5) (c) Hydrogen Sulfide	Hydrogen Sulfide may not be emitted from any process stream which contains H_2S in concentrations greater than 15 grains per 100 cubic feet of gas without burning or removing H_2S in excess of this concentration. This limitation is acceptable provided that the final SO_x emission limitations are not violated.

feet of gas before burning or flaring. The most stringent limitation, 15 grains per 100 cubic feet of gas, was promulgated by the State of Virginia. The purpose of this regulation is to achieve acceptable ambient air levels of sulfur oxide emissions.

Water Pollution Control Standards

Water Quality Criteria

The states' water quality criteria/standards usually consist of water use classifications, water use descriptions and specific standards, as well as general water quality criteria. The specific water quality standards which are applicable to a given area depend on the water use classification that may be assigned to an area.

A review was made of the five major coke producing states to examine specific water quality criteria applicable to coke oven emissions. Based on published state regulations and The Bureau of National Affairs (BNA) publications on state water laws at the time of this writing (current to 1976), only Pennsylvania and West Virginia had published promulgated criteria.

Solid Waste Disposal Standards

Hazardous Waste Handling and Disposal

The EPA is delegating the enforcement authority under the "Resource Conservation and Recovery Act of 1976" to the states. Although the specific regulations for the handling, transport and disposal have not been promulgated by the EPA, some states such as Pennsylvania have already implemented their own hazardous materials transporting and disposal regulations.

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APPENDIX A. SI (METRIC) CONVERSION FACTORS

To Convert From	To	Multiply By
	Acceleration	
ft/s^2	meter per $second^2$ (m/s^2)	3.048-000 E-01
	Area	
Acre (U.S. survey)[12]	$meter^2$ (m^2)	4.046 873 E+03
ft^2	$meter^2$ (m^2)	9.290 304 E-02
in^2	$meter^2$ (m^2)	6.451 600 E-04
yd^2	$meter^2$ (m^2)	8.361 274 E-01
	Energy (Includes Work)	
British thermal unit (mean)	joule (J)	1.055 87 E+03
Calorie (kilogram, mean)	joule (J)	4.190 02 E+03
Kilocalorie (mean)	joule (J)	4.190 02 E+03
	Length	
foot	meter (m)	3.048 000 E-01
inch	meter (m)	2.540 000 E-02
yard	meter (m)	9.144 000 E-01
	Mass	
grain	kilogram (kg)	6.479 891 E-05
grain	kilogram (kg)	1.000 000 E-03
pound (lb avoirdupois)	kilogram (kg)	4.535 924 E-01
ton (metric)	kilogram (kg)	1.000 000 E+03
ton (short, 2000 lb)	kilogram (kg)	9.071 847 E+02
	Mass Per Unit Area	
lb/ft^2	kilogram per $meter^2$ (kg/m^2)	4.882 428 E+00

APPENDIX A (Continued)

To Convert From	To	Multiply By
	Temperature	
degree Celsius	Kelvin (K)	$t_K = t_{^\circ C} + 273.15$
degree Fahrenheit	degree Celsius	$t_{^\circ C} = (t_{^\circ F} - 32)/1.8$
degree Fahrenheit	Kelvin (K)	$t_K = (t_{^\circ F} + 459.67)/1.8$
degree Rankine	Kelvin (K)	$t_K = t_{^\circ R}/1.8$
Kelvin	degree Celsius	$t_{^\circ C} = t_K - 273.15$
	Velocity (Includes Speed)	
ft/h	meter per second (m/s)	8.466 667 E-05
ft/min	meter per second (m/s)	5.080 000 E-03
ft/s	meter per second (m/s)	3.048 000 E-01
in/s	meter per second (m/s)	2.540 000 E-02
	Viscosity	
centipoise	pascal second (Pa.s)	1.000 000 E-03
centistokes	meter^2 per second (m^2/s)	1.000 000 E-06
poise	pascal second (Pa.s)	1.000 000 E-01
stokes	meter^2 per second (m^2/s)	1.000 000 E-04
	Volume (Includes Capacity)	
acre-foot (U.S. survey)	meter^3 (m^3)	1.233 489 E+03
barrel (oil, 42 gal)	meter^3 (m^3)	1.589 873 E-01
ft^3	meter^3 (m^3)	2.831 685 E-02
gallon (U.S. liquid)	meter^3 (m^3)	3.785 412 E-03
liter*	meter^3 (m^3)	1.000 000 E-03
	Volume Per Unit Time (Includes Flow)	
ft^3/min	meter^3 per second (m^3/s)	4.719 474 E-04
ft^3/s	meter^3 per second (m^3/s)	2.831 685 E-02
gal (U.S. liquid/day)	meter^3 per second (m^3/s)	4.381 264 E-03
gal (U.S. liquid/min)	meter^3 per second (m^3/s)	6.309 020 E-05

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*In 1964 the General Conference on Weights and Measures adopted the name liter as a special name for the cubic decimeter. Prior to this decision the litre differed slightly (previous value, 1.000028 dm^3) and in expression of precision volume measurement this fact must be kept in mind.

APPENDIX A (Continued)

To Convert From	To	Multiply By
	Mass Per Unit Length	
lb/ft	Kilogram per meter (kg/m)	1.488 164 E+00
lb/in	Kilogram per meter (kg/m)	1.785 797 E+01
	Mass Per Unit Time (Includes Flow)	
lb/h	Kilogram per second (kg/s)	1.259 979 E-04
lb/min	Kilogram per second (kg/s)	7.559 873 E-03
ton (short)/h	Kilogram per second (kg/s)	2.519 958 E-01
	Mass Per Unit Volume (Includes Density & Mass Capacity)	
lb/ft^3	Kilogram per meter^3 (kg/m^3)	1.601 846 E+01
lb/gal (U.S. liquid)	Kilogram per meter^3 (kg/m^3)	1.198 264 E+02
lb/yd^3	Kilogram per meter^3 (kg/m^3)	5.932 764 E-01
	Power	
Btu (Thermochemical)/h	Watt (w)	2.930 711 E-01
Btu (thermochemical)/h	Watt (W)	2.928 751 E-01
cal (thermochemical)/min	Watt (w)	6.973 333 E-02
cal (thermochemical)/s	Watt (W)	4.184 000 E+00
	Pressure or Stress (Force Per Unit Area)	
atmosphere (standard)	pascal (Pa)	1.013 250 E+05
foot of water (39.2°F)	pascal (Pa)	2.988 98 E+03
lbf/ft^2	pascal (Pa)	4.788 026 E+01
lbf/in^2 (psi)	pascal (Pa)	6.894 757 E+03